Synthesis of mesoionic carbene-triazole based Pd(II) complex: promoting C-H activation toward N-aryl carbazoles

Puneet Singh Gahlaut,[1†] Bhawana Shekhawat,[1†] Prem Lama,[2] and Barun Jana[*1]

Supporting Information

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1. Experimental Section

1.1 General information

All the experiments were conducted under an ambient condition only if specifically stated to the use of an inert atmosphere. All the chemicals and solvents were used as received from the suppliers without further purification. Reagents, 2-bromopyridine (99%), propargyl bromide (87%), p cresol (99%) were purchased from Spectrochem, India. Solvents hexane, ethyl acetate was purchased from Finar limited company. Normal (particle size: 100–200 mesh) and flash (particle size: 230–400 mesh) silica gels were used for column chromatography, and they were purchased from Qualigens-TM (India), Spectrochem (India), and Rankem (India). To monitor the progress of chemical reactions, TLC plates covered with silica gel (Kiesel 60-F254, Merck (India)) were utilized. UV light was the visualizing agent that was used for TLC. All the solvents were dried and concentrated using D LAB Rotavapor RE 100-

S. The supplied analytical-grade solvents, such as MeOH and EtOH, were all utilized without any previous purification. The chemicals and reagents acquired from Sigma Aldrich Chemicals Company (USA), TCI (India) Pvt. Ltd., Merck (India), and/or Spectrochem (India), were utilized as received. Deuterated solvent $CDCl_3$ and DMSO-d_6 were used to record the NMR spectrum of the synthesized compounds.

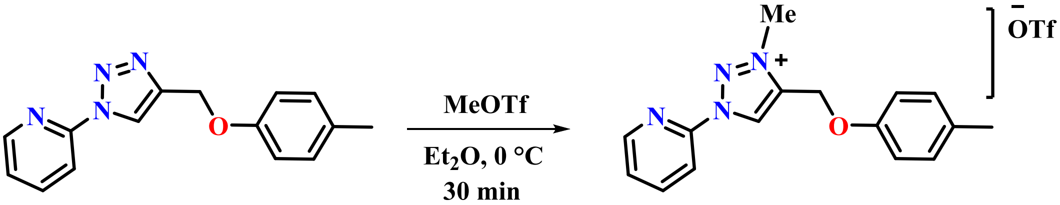
1.2 Instrumentation

Nuclear magnetic resonance spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 MHz for ^1H NMR and 101 MHz for $^{13}C\{^1H\}$ NMR respectively. Tetramethyl silane (TMS) (0.00 ppm) was used as a reference internal solvent to record ^1H and $^{13}C\{^1H\}$ NMR spectra for all the compounds. During analysis of ^1H NMR spectra proton peak for $CDCl_3$ was fixed at 7.246 ppm and the carbon peak was fixed at 77.0 ppm. ^1H NMR patterns of chemical shifts were characterized in parts per million (ppm). The terms singlet (s), doublet (d), double of doublet (dd), triplet (t), and multiplet (m) were used to describe peak splitting patterns. The coupling constant (J) values are given in Hertz (Hz). The Xevo G2-SQ-Tof (Waters, USA) was used to examine high-resolution electron impact mass spectra (HR-EIMS), which are compatible with ACQUITY UPLC® and nano ACQUITY UPLC® systems. UV/vis absorption measurements were conducted at room temperature on a SHIMADZU UV-19000I UV/vis spectrophotometer. The melting point of ligand and complex were determined on an analog melting point apparatus. IR spectra were recorded on a FTIR–03130 Shimadzu Spectrophotometer in ATR mode. The melting point of ligand and complex were determined on an analog melting point apparatus. The Bruker single crystal X-ray diffractometer was used to determine the crystallography study of Pd-complex.

2. Synthesis and characterization of ligand (Me-tmtp) and Pd-MIC complex:

2.1 3-methyl-1-(pyridin-2-yl)-4-((p-tolyloxy)methyl)-1H-1,2,3-triazol-3-ium (Me-tmtp):

The ligand 3-methyl-1-(pyridin-2-yl)-4-((p-tolyloxy)methyl)-1H-1,2,3-triazol-3-ium was synthesized by stirring at 0 °C in a round-bottom flask on a magnetic stirrer. In a round bottom flask 2-(4-((p-tolyloxy)methyl)-1H-1,2,3-triazol-1-yl)pyridine (0.200 g, 1 mmol) solution was made in diethyl ether at 0 °C temperature. Then methyl trifluoromethansulfonate (1.2 mmol) was dropwise added to the solution and the resulting solution was stirred for 30 min. After the reaction had reached completion, the workup was done with water (10 mL) and ethyl acetate (3 × 20 mL). Then, the combined organic layers were dried using anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to afford the crude residue that was further purified utilizing column chromatography on silica gel (100–200 mesh) (99:1 - Chloroform/MeOH). The solvent was removed under reduced pressure and off-white crystalline solid of product was obtained. Yield: 83% (0.175 g), based on 2-(4-((p-tolyloxy)methyl)-1H-1,2,3-triazol-1-yl)pyridine. Mp: 160-165 °C. ^{1}H NMR (400 MHz, Acetonitrile-D_3) δ 9.22 (s, 1H), 8.68 – 8.66 (m, 1H), 8.22-8.17 (m, 1H), 8.10 – 8.07 (m, 1H), 7.74 – 7.71 (m, 1H), 7.20-7.18 (m, 2H), 7.02-6.98 (m, 2H), 5.40 (s, 2H), 4.42 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D_6) δ 155.4, 150.0, 146.8, 141.7, 141.0, 131.5, 130.6, 127.8, 127.3, 115.6, 115.3, 61.1, 58.4, 20.6. HRMS (ESI+) [$C_{16}H_{17}N_4O^+$]m/z calcd. for $[M + H]^+$ 281.1397; found 281.1395. IR υ_{max} (cm^{-1}): 3100 (m, Csp2-H stretch.), 3010 (w, triazole), 2928 (m, Csp3-H stretch.), 1513 (m, Csp3-H stretch.), 1256 (s, Csp3-O stretch.), 803 (s, C=Csp2 bend). UV-vis. $\lambda_{max.}$ (nm): 271.98 (n-π^*), 222.66 (π-π^*).



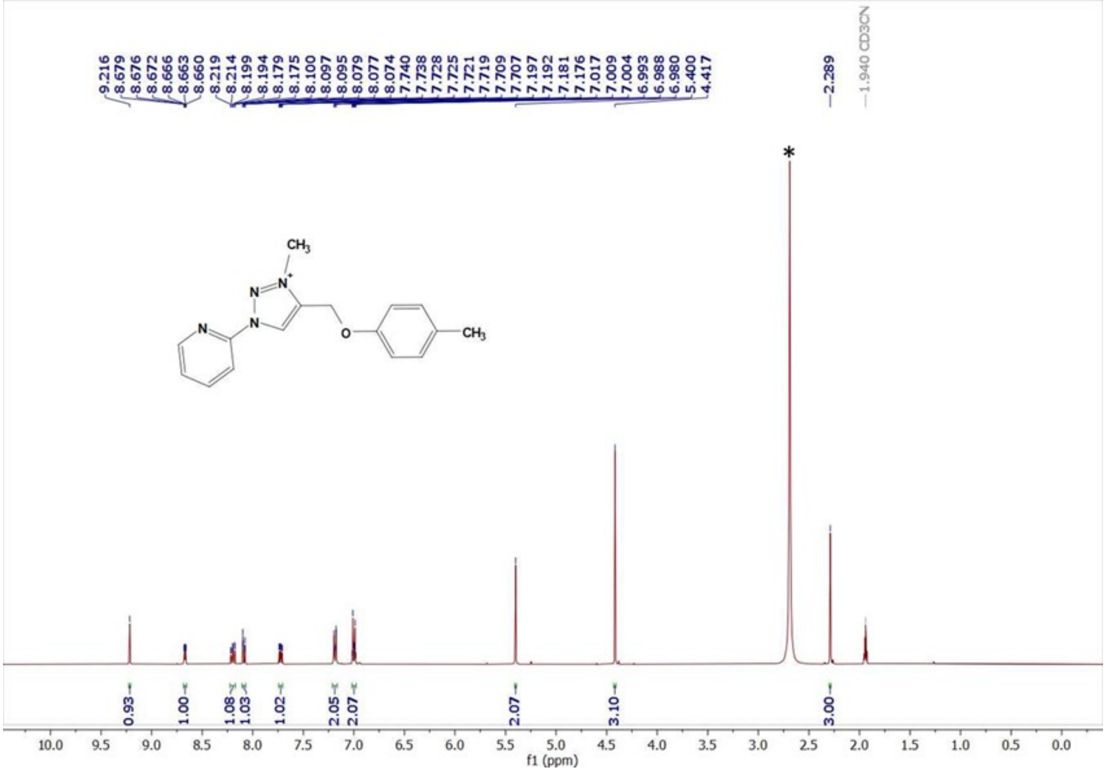


Fig. S1: ^{1}H-NMR spectra of ligand (Me-tmtp) [400 MHz] {*Residual CH_3CN}

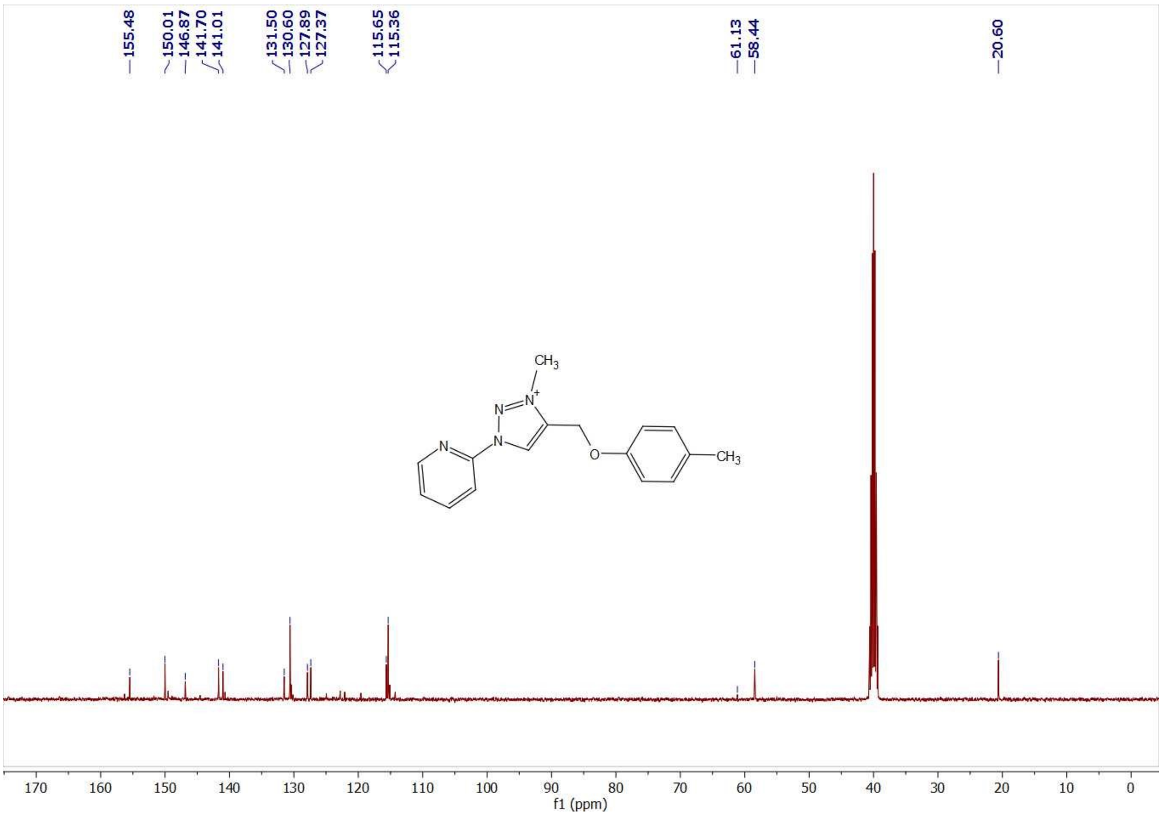
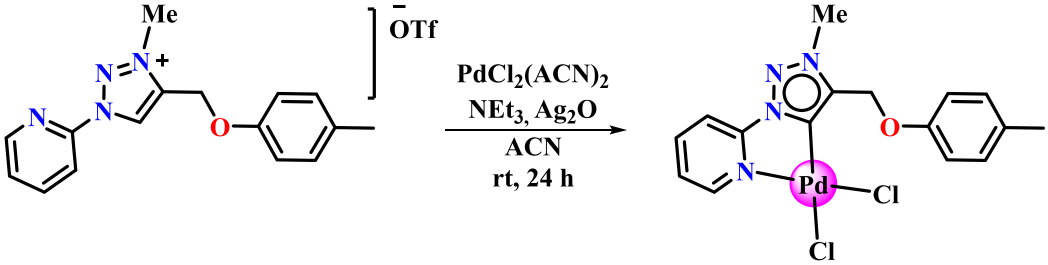


Fig. S2: ^{13}C-NMR spectra of ligand (Me-tmtp) [101 MHz]

2.2 Synthesis Pd-MIC complex and characterization

For the synthesis of Pd-MIC complex, the Me-tmtp ligand (0.100g, 1 mmol) solution was made in ACN, (2 ml) in a 50 ml round bottom flask and then add Ag_2O (1 mmol) with 25 µL of NEt_3. The reaction mixture was stirred at RT with the exclusion of light for 24 h. The solution was filtered and evaporated. Now, the suspension was dissolved in dry ACN and then add $[PdCl_2(CH_3CN)_2]$ (1.00 mmol) after that the reaction further stirred at RT for 14 h. Then reaction mixture was filtered using a Buchner funnel. Now Pd-MIC complex was then precipitated from a DCM/Hexane mixture as a brown yellowish solid was obtained as product. Yield: 63% (0.102 g), based on ligand (Me-tmtp). Mp: 219-222 °C. ^{1}H NMR (400 MHz, DMSO-D$_6$) δ 9.84-9.80 (m, 1H), 9.57- 9.54 (m, 1H), 9.20-9.17 (m, 1H), 8.47 – 8.31 (m, 3H), 7.07 – 6.83 (m, 2H), 5.73 (s, 2H), 4.71 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*D*$_6$) δ 155.6, 149.7, 147.5, 144.7(Pd-C), 141.5, 137.2, 131.1, 130.5, 127.5, 115.3, 114.8, 58.2, 46.2, 20.6. HRMS (ESI+) $[C_{16}H_{18}Cl_2N_4OPd]$ m/z calcd. for $[M+Na]^+$ 480.9789; found 480.9762. IR υ_{max} (cm^{-1}): 3102 (m, Csp2-H stretch.), 3080 (m, triazole) 2922 (m, Csp3-H stretch.), 1256 (s, Csp3-O stretch), 803 (m, C=Csp2 bend). UV-vis. $\lambda_{max.}$ (nm): 277.58 (n-π*).



Pd-MIC complex

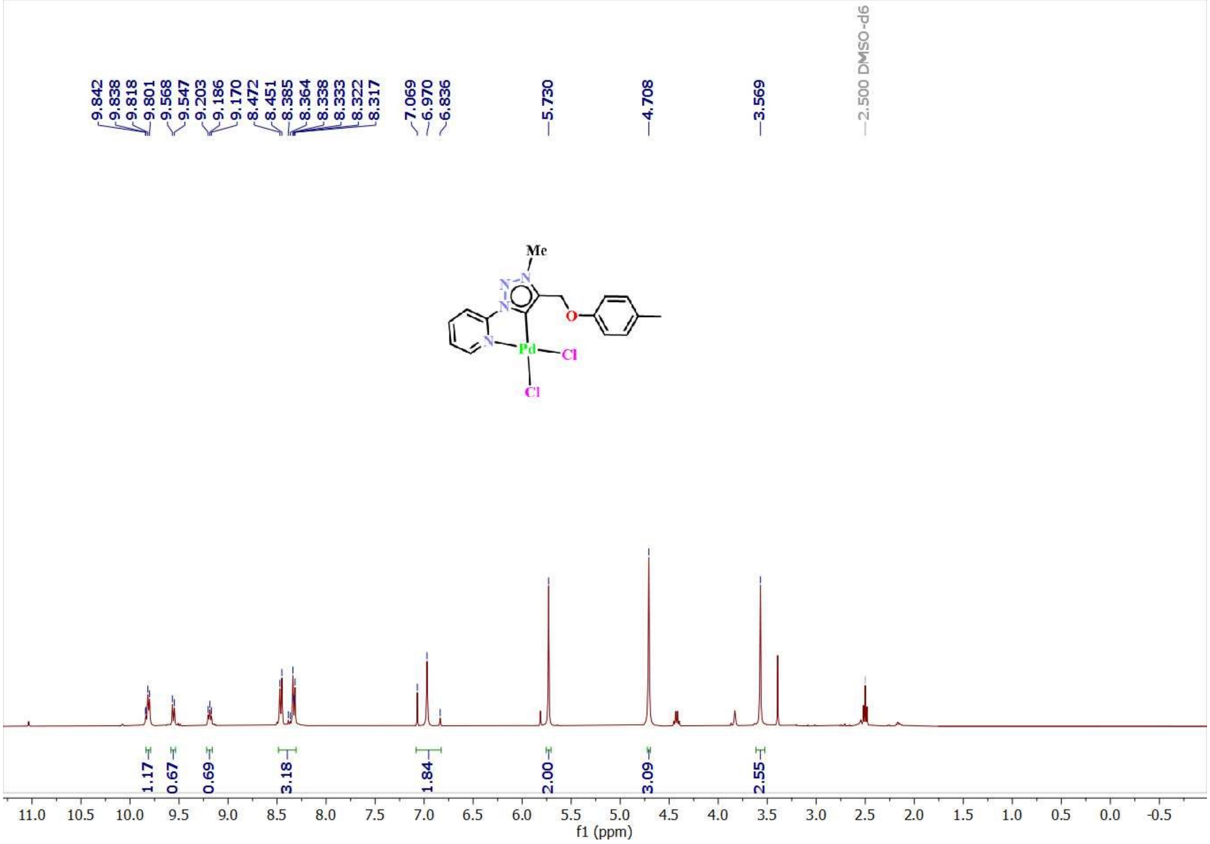


Fig. S3: ^{1}H-NMR spectra of Pd-MIC complex [400 MHz]

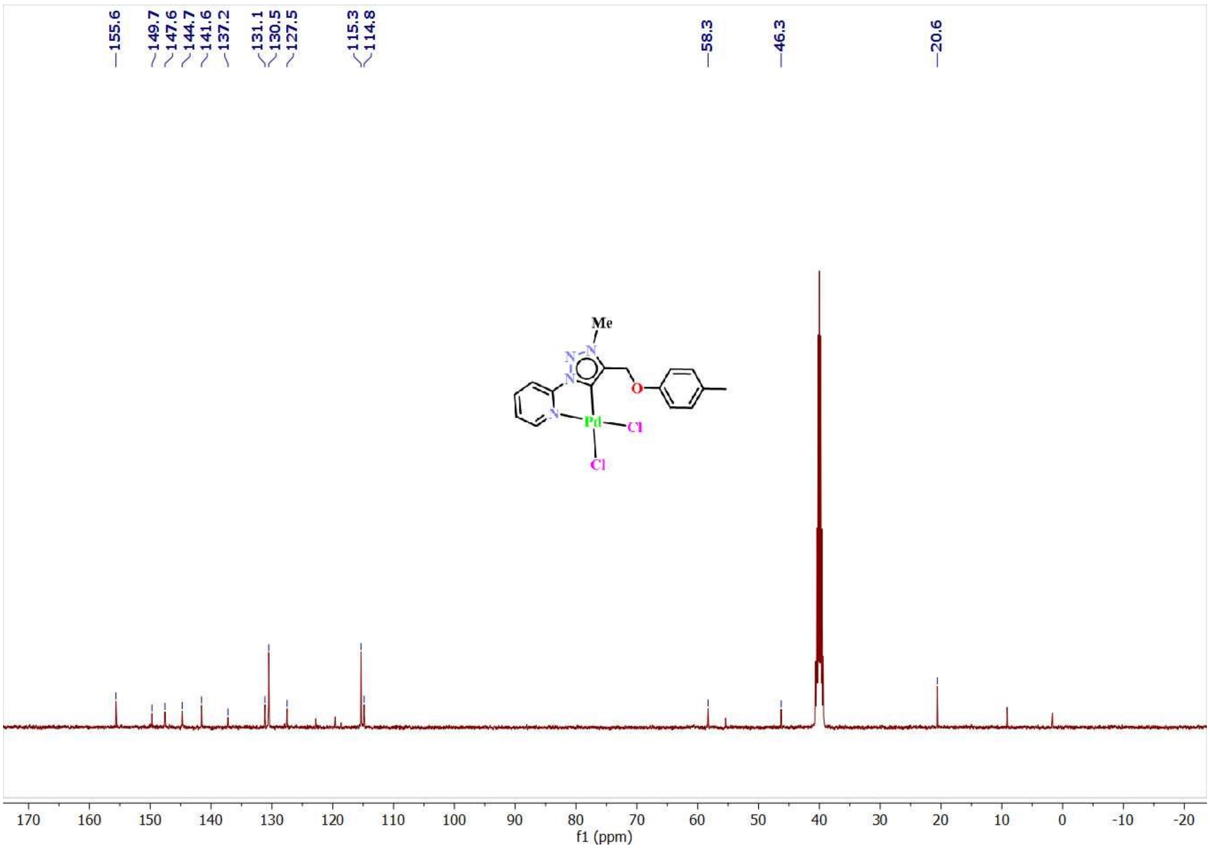


Fig. S4: ^{13}C-NMR spectra of Pd-MIC complex [101 MHz]

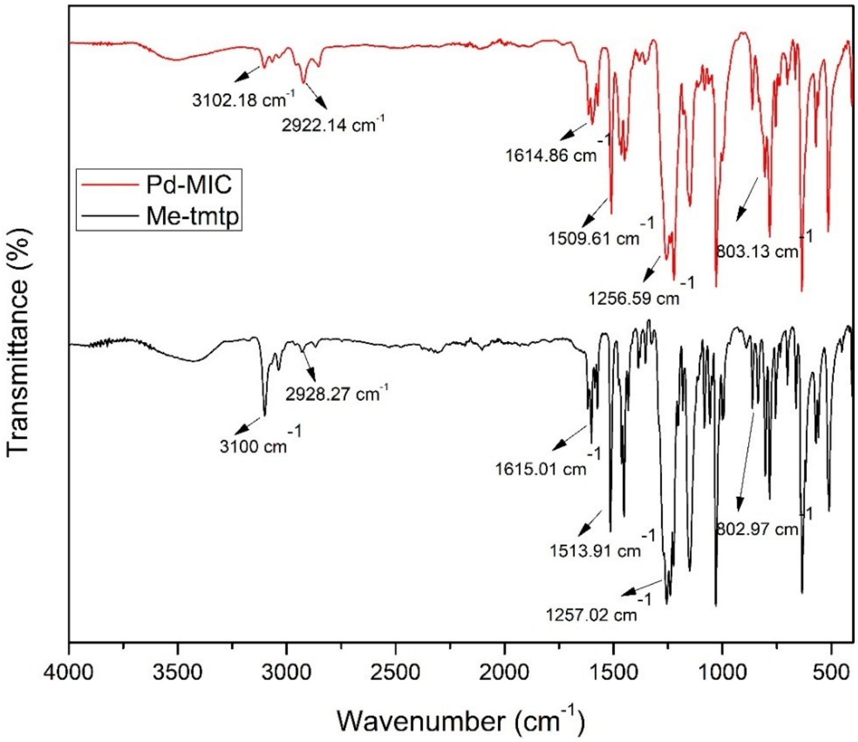


Fig. S5: Comparative FTIR spectra of ligand (Me-tmtp) and Pd-MIC complex

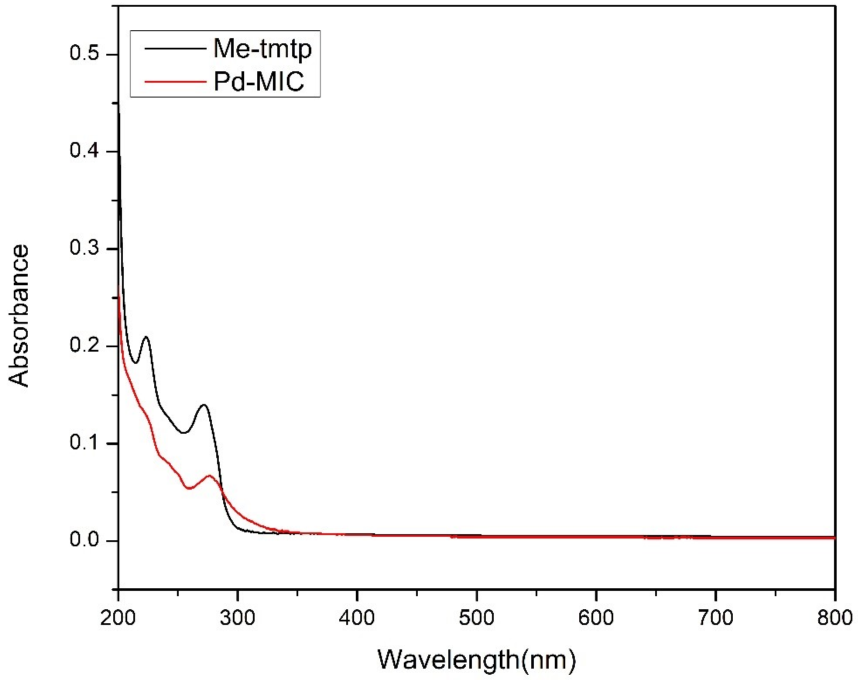


Fig. S6: Comparative UV-Visible spectra of ligand (Me-tmtp) and Pd-MIC complex

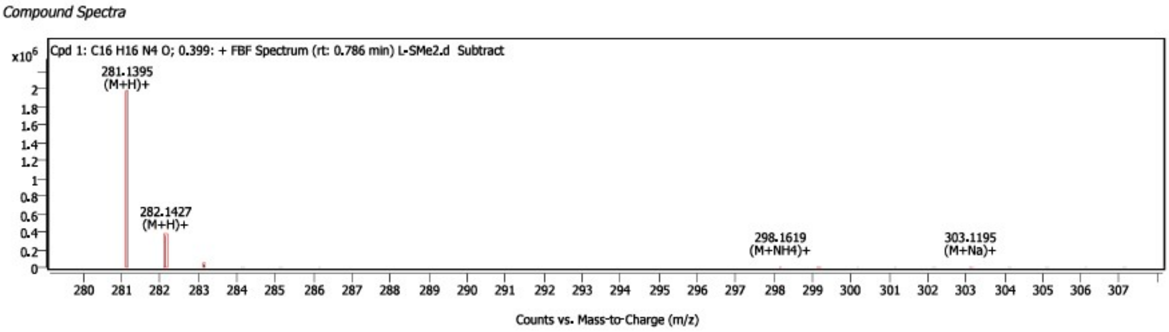


Fig. S7: ESI(+ve) mass data of ligand (Me-tmtp)

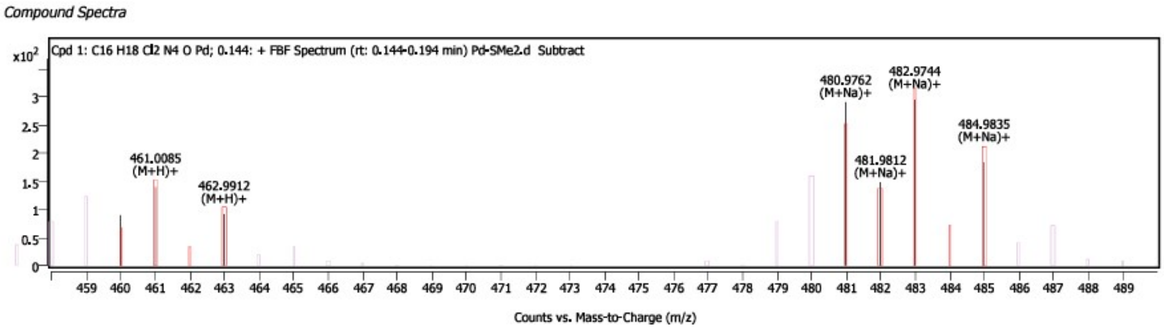


Fig. S8: ESI(+ve) mass data of Pd-MIC complex

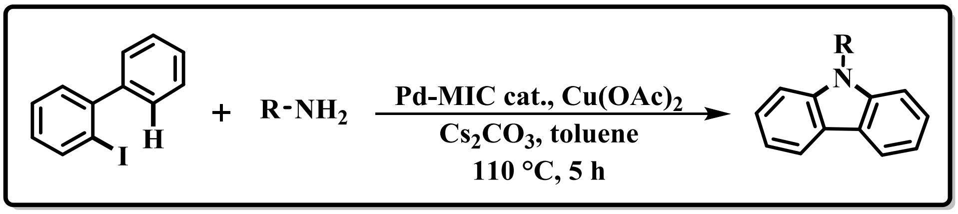
Table S1: Crystal Data and structure refinement for Pd-complex:

CCDC number	**2516819**
Empirical formula	$C_{16}H_{16}Cl_2N_4OPd$
Formula weight	457.65
Temperature [K]	100
Crystal system	monoclinic
Space group (number)	$P2_1/c$
a [Å]	9.0409(10)
b [Å]	7.1271(8)
c [Å]	27.278(3)
α [°]	90
β [°]	95.896(3)
γ [°]	90
Volume [Å^3]	1748.4(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.739
μ [mm^{-1}]	1.378
F(000)	909.7
Crystal size [mm^3]	0.26×0.22×0.2
Crystal colour	brown
Crystal shape	needle
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	5.92 to 50
Index ranges	$-10 \leq h \leq 10$ $-8 \leq k \leq 8$ $-32 \leq l \leq 32$
Reflections collected	29877
Independent reflections	3082 R_{int} = 0.0560 R_{sigma} = 0.0341

Data / Restraints / Parameters	3082 / 0 / 219
Goodness-of-fit on F^2	1.441
Final R indexes [I≥2σ(I)]	R_1 = 0.0555, wR_2 = 0.0984
Final R indexes [all data]	R_1 = 0.0582, wR_2 = 0.0993
Largest peak/hole [eÅ^{-3}]	0.91/−1.78

3 General procedure for the synthesis of N-substituted carbazoles

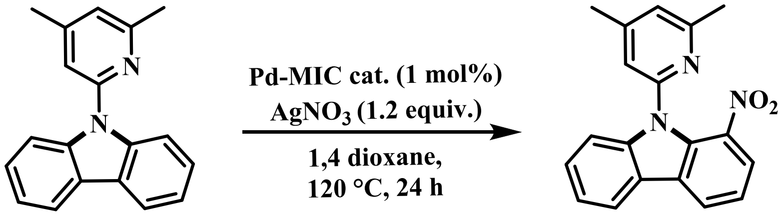
A dry sealed tube equipped with magnetic stirrer was charged with 2-iodobiphenyls (0.5 mmol), aromatic amines (0.56 mmol), $Cu(OAc)_2$ (0.5 mmol), Cs_2CO_3 (0.5 mmol), Pd-catalyst (0.5 mol%) and toluene (2 mL). The reaction mixture was sealed and stirred at 110 °C for 5 hours and then cooled at room temperature. Water (10 mL) was added to the resultant mixture. The product was extracted with ethyl acetate (10 mL × 3), and the combined organic layers were washed with brine (10 mL × 2) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified *via* silica gel chromatography (230-400 mesh particle size) in hexane to afford the desired N-substituted carbazoles.



4 Post Synthetic Application:

4.1 Nitration of N-substituted carbazoles:

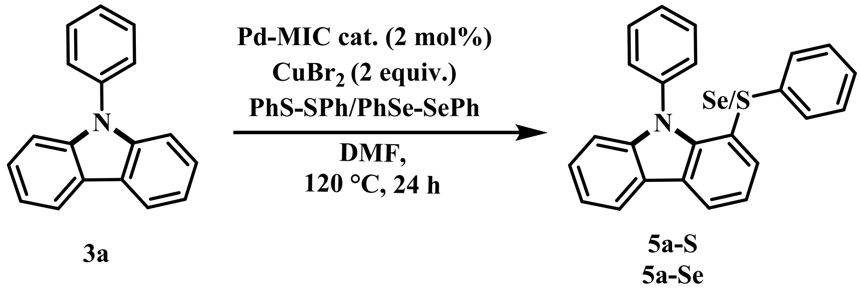
A 15 mL pressure tube was charged with Pd-MIC catalyst (1 mol %), 9-(3,5-dimethylpyridin-2-yl)-9*H*-carbazole (0.2 mmol), and $AgNO_3$ (0.24 mmol). Then, the solvent 1,4-dioxane (2.0 mL) was added, and the reaction mixture was allowed to stir in a preheated oil bath at 120 °C for 24 h. Upon completion of the reaction time, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 mL). The reaction mixture was filtered through a Celite pad, and the filtrate was concentrated using a rotary evaporator. The crude residue was purified through silica gel column chromatography using n-hexane/EtOAc 98:2 as eluent to give the pure C1-nitrated carbazole **4a** with 45% (0.052 g) yield.



3j **4a**

4.2 Chalcogenation of N-substituted carbazoles:

A 15 mL pressure tube was charged with Pd-MIC catalyst (2 mol %), 9-phenyl-9*H*-carbazole (0.3 mmol), diphenyl disulfide/diphenyl diselenide (0.3 mmol) and $CuBr_2$ (0.6 mmol). Then, the solvent DMF (2.0 mL) was added, and the reaction mixture was allowed to stir in a preheated oil bath at 120 °C for 24 h. The reaction was cooled to room temperature, filtered through a plug of Celite, and then washed with ethyl acetate (10 mL × 3). The solvents were removed under reduced pressure, and the crude reaction mixture was purified by silica gel column chromatography using n-hexane as an eluent to give the desired product with good yield [**5a-S** (70%, 0.101 g) and **5a-Se** (75%, 0.123 g)].



4.3 Hot Filtration Test:

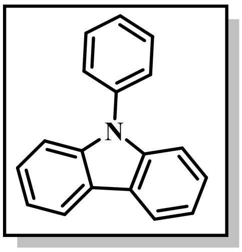
In the starting we have run the model reaction normally until partial conversion occurs. While the reaction mixture is still hot, quickly filter it to remove any insoluble solids (metal catalyst or any other impurities). Further heating and stirring the clear solution under the same reaction conditions. After the completion of the reaction, we get our desired product in the same amount of yield. This confirms the Pd-MIC catalyst is likely homogenous.

5 Comparative Table:

Catalyst	Reaction conditions	References
Fluorescent lamp (23 W)	2-azidobiphenyls, silica gel (15 mg), H_2O/Acetone (1/1), 28 °C to 32 °C, 48 h	1
$Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%)	Aniline, Dichloroarene, K_3PO_4 (3 equiv.), NMP, 130 °C, 18 h	2
$Pd(OAc)_2$ (5 mol%)	2-iodobiphenyls, Diaziridinone, Cs_2CO_3 (1 equiv.), KOAc (0.5 equiv.), DMF, N_2, 110 °C, 6 h	3
$Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%)	2-iodobiphenyls, Aniline, $Cu(OAc)_2$ (1 equiv.), Cs_2CO_3 (1 equiv.), DMF, Air, 120 °C, 12 h	4
Our work	**Pd-MIC (0.25 mol%), 2-iodobiphenyls, Aniline, $Cu(OAc)_2$ (1 equiv.), Cs_2CO_3 (1 equiv.), Toluene, 110 °C, 5 h**	

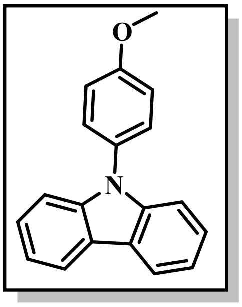
6 Characterization data of N-substituted carbazoles:

9-phenyl-9*H*-carbazole (3a)



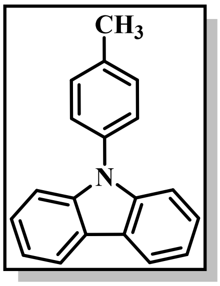
Yield- 0.078 g, 90%. White solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.39-7.37 (m, 2H), 6.82-6.77 (m, 4H), 6.68 – 6.61 (m, 5H), 6.54 – 6.50 (m, 2H). Spectral data are in good agreement with literature values[4].

9-(4-methoxyphenyl)-9*H*-carbazole (3b)



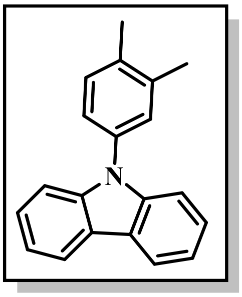
Yield- 0.073 g, 75%. White solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.41 – 7.35 (m, 4H), 7.30 – 7.26 (m, 1H), 7.13-7.09 (m, 2H), 7.06-7.04 (m, 1H), 6.98 – 6.95 (m, 2H), 6.77 – 6.75 (m, 2H), 3.71 (s, 3H). Spectral data are in good agreement with literature values[5].

9-(p-tolyl)-9*H*-carbazole (3c)



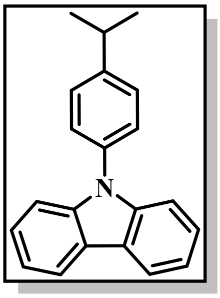
Yield- 0.064 g, 70%. White solid. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.16-8.14 (m, 2H), 7.45 – 7.38 (m, 8H), 7.30-7.27 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 141.1, 137.4, 135.1, 130.6, 127.1, 125.9, 123.3, 120.4, 119.8, 109.9, 21.4. Spectral data are in good agreement with literature values[4].

9-(3,4-dimethylphenyl)-9*H*-carbazole (3d)



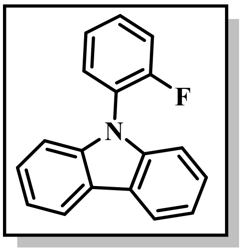
Yield- 0.050 g, 52%. White solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.15-8.13 (m, 2H), 7.40 – 7.32 (m, 6H), 7.29 – 7.25 (m, 3H), 2.39 (s, 3H), 2.36 (s, 3H). Spectral data are in good agreement with literature values[4].

9-(4-isopropylphenyl)-9*H*-carbazole (3e)



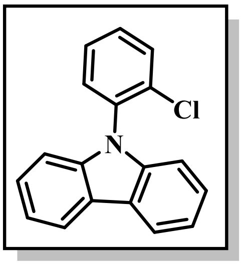
Yield- 0.066 g, 65%. White solid. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.15-8.13 (m, 2H), 7.46 – 7.40 (m, 8H), 7.28-7.25 (m, 2H), 3.07-3.01 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 148.3, 141.2, 135.3, 127.9, 127.1, 125.9, 123.3, 120.3, 119.8, 109.9, 34.0, 24.1. Spectral data are in good agreement with literature values[4].

9-(2-fluorophenyl)-9*H*-carbazole (3f)



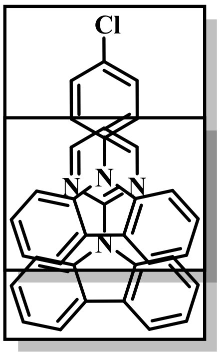
Yield- 0.078 g, 84%. White solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.17-8.15 (m, 2H), 7.70 – 7.67 (m, 1H), 7.53 – 7.47 (m, 3H), 7.43-7.39 (m, 2H), 7.32-7.28 (m, 2H), 7.11-7.08 (m, 2H). Spectral data are in good agreement with literature values[6].

9-(2-chlorophenyl)-9*H*-carbazole (3g)



Yield- 0.049 g, 50%. White solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.15-8.13 (m, 2H), 7.59-7.55 (m, 1H), 7.52 – 7.46 (m, 1H), 7.44 – 7.34 (m, 4H), 7.32 – 7.28 (m, 2H), 7.25 – 7.22 (m, 2H). Spectral data are in good agreement with literature values[4].

9-(4-chlorophenyl)-9*H*-carbazole (3h)

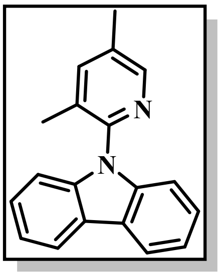


Yield- 0.079 g, 80%. White solid. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.15 – 8.13 (m, 2H), 7.58-7.56 (m, 2H), 7.51-7.50 (m, 2H), 7.41-7.40 (m, 2H), 7.37 – 7.35 (m, 2H), 7.31 – 7.29 (m, 2H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 140.8, 136.4, 133.1, 130.2, 128.5, 126.2, 123.6, 120.5, 120.3, 109.6. Spectral data are in good agreement with literature values[4].

9-(pyrimidin-2-yl)-9*H*-carbazole (3i)

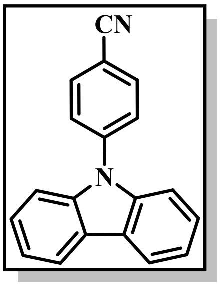
Yield- 0.039 g, 45%. Brown solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.85- 8.83 (m, 4H), 8.08- 8.06 (m, 2H), 7.52- 7.48 (m, 2H), 7.38 - 7.34 (m, 2H), 7.12 (t, *J* = 4.8 Hz, 1H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 158.0, 139.2, 126.7, 125.9, 122.4, 119.6, 116.3, 116.1. HRMS (ESI+) [$C_{16}H_{11}N_3$] m/z calcd. for $[M+H]^+$246.1031; found 246.1026.

9-(3,5-dimethylpyridin-2-yl)-9*H*-carbazole (3j)



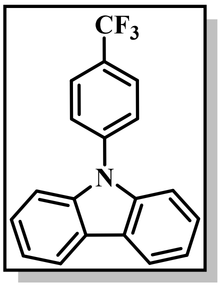
Yield- 0.062 g, 64%. Brown solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.12- 8.09 (m, 2H), 7.81- 7.79 (m, 2H), 7.44- 7.41 (m, 2H), 7.31-7.27 (m, 2H), 7.25- 7.23 (m, 1H), 7.00- 6.99 (m, 1H), 2.63 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.4, 150.1, 149.0, 138.6, 125.0, 123.1, 120.9, 119.5, 119.1, 115.7, 110.2, 23.2, 20.1. HRMS (ESI+) [$C_{19}H_{16}N_2$] m/z calcd. for $[M+H]^+$ 273.1391; found 273.1386.

4-(9*H*-carbazol-9-yl)benzonitrile (3k)



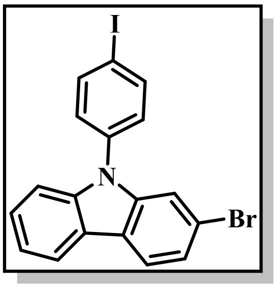
Yield- 0.072 g, 75%. White solid. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.54 – 7.50 (m, 6H), 7.43-7.41 (m, 2H), 7.21 – 7.19 (m, 4H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 145.6, 138.7, 132.1, 130.7, 130.6, 129.0, 118.7, 111.0. Spectral data are in good agreement with literature values[4].

9-(4-(trifluoromethyl)phenyl)-9*H*-carbazole (3l)



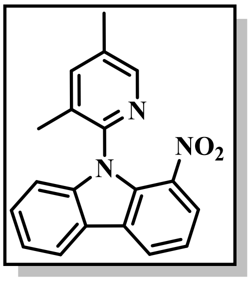
Yield- 0.092 g, 83%. White solid. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.42 (m, 4H), 7.34-7.30 (m, 2H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 141.2, 140.4, 127.2, 127.2, 127.2, 126.3, 123.8, 120.7, 120.6, 109.7. Spectral data are in good agreement with literature values[5]. C–F coupling patterns were not clearly resolved[7].

2-bromo-9-(4-iodophenyl)-9*H*-carbazole (3m)



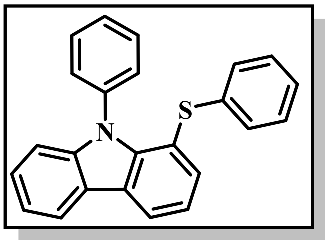
Yield- 0.062 g, 50%. White solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.08 (d, J = 7.7 Hz, 1H), 7.56 – 7.48 (m, 3H), 7.40 – 7.38 (m, 1H), 7.35 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 7.16-7.12 (m, 1H), 7.10 – 7.08 (m, 1H). Spectral data are in good agreement with literature values[6].

9-(3,5-dimethylpyridin-2-yl)-1-nitro-9*H*-carbazole (4a)



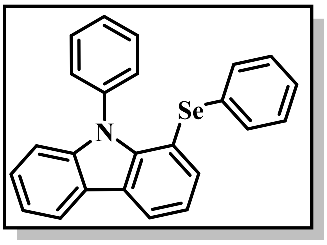
Yield- 0.058 g, 50%. Yellow solid. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.28-8.25 (m, 1H), 8.07 – 8.04 (m, 1H), 7.93-7.91 (m, 1H), 7.55-7.52 (m, 1H), 7.43 – 7.39 (m, 1H), 7.32 – 7.26 (m, 2H), 7.18 – 7.17 (m, 1H), 6.94 – 6.93 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 158.4, 150.8, 150.5, 141.6, 136.8, 131.5, 128.6, 127.7, 125.2, 123.5, 123.1, 122.5, 122.0, 120.5, 120.0, 117.4, 111.0, 24.0, 21.3. HRMS (ESI+) [$C_{19}H_{15}N_3O_2$] m/z calcd. for $[M+H]^+$ 318.1242; found 318.1274.

9-phenyl-1-(phenylthio)-9*H*-carbazole (5a-S)



Yield- 0.101 g, 70%. Colourless liquid. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 8.25 (d, *J* = 1.9 Hz, 1H), 8.10-8.08 (m, 1H), 7.62-7.59 (m, 3H), 7.53 – 7.46 (m, 6H), 7.44 – 7.40 (m, 2H), 7.32 – 7.23 (m, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 141.3, 139.6, 137.3, 130.1, 128.7, 127.9, 127.1, 126.8, 125.2, 123.2, 122.4, 120.6, 120.4, 112.8, 111.4, 110.1. HRMS (ESI+) [$C_{24}H_{17}NS$] m/z calcd. for $[M+H]^+$ 352.1164; found 352.1175.

9-phenyl-1-(phenylselanyl)-9*H*-carbazole (5a-Se)



Yield- 0.119 g, 73%. Colourless liquid. ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 8.34 (d, J = 1.6 Hz, 1H), 8.19 (d, J = 1.9 Hz, 1H), 7.65 – 7.59 (m, 3H), 7.52 – 7.47 (m, 4H), 7.37 – 7.31 (m, 3H), 7.26 – 7.19 (m, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 141.3, 140.8, 137.4, 134.2, 133.4, 130.5, 130.1, 129.3, 128.1, 127.9, 127.2, 126.6, 126.3, 124.7, 122.8, 120.6, 120.5, 119.0, 111.0, 110.1. HRMS (ESI+) [$C_{24}H_{17}NSe$] m/z calcd. for $[M+H]^+$ 400.0604; found 400.0568.

7 Spectral data of N-substituted carbazoles:

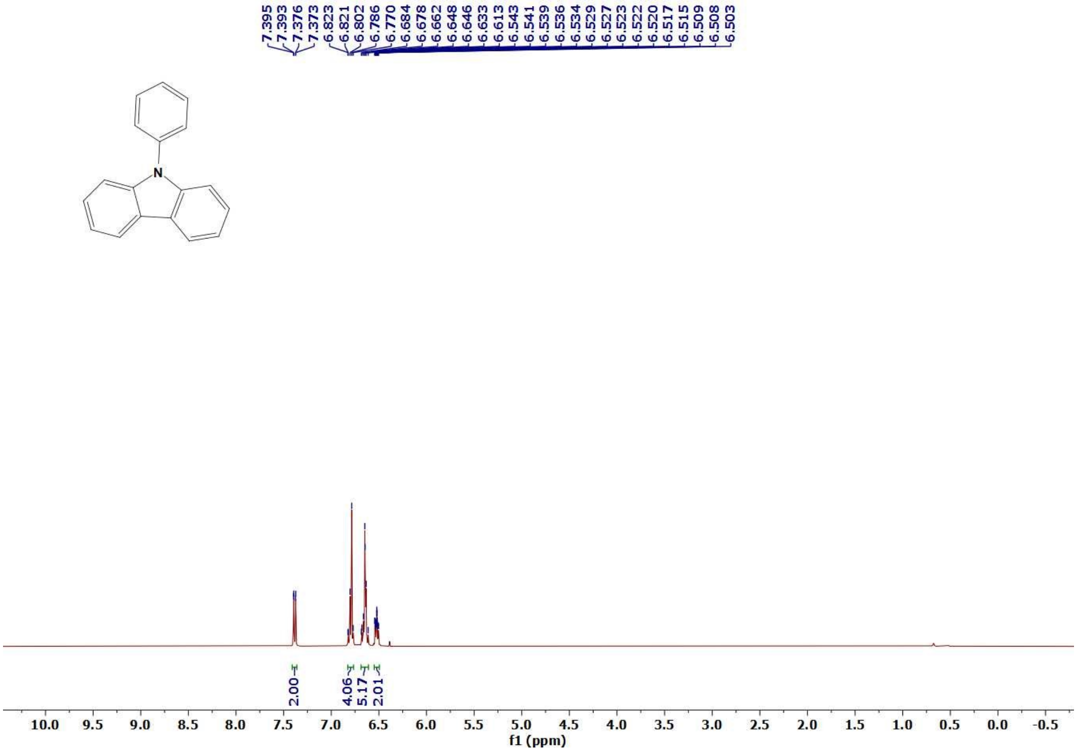


Fig. S9: ^{1}H-NMR spectra of 3a compound [400 MHz]

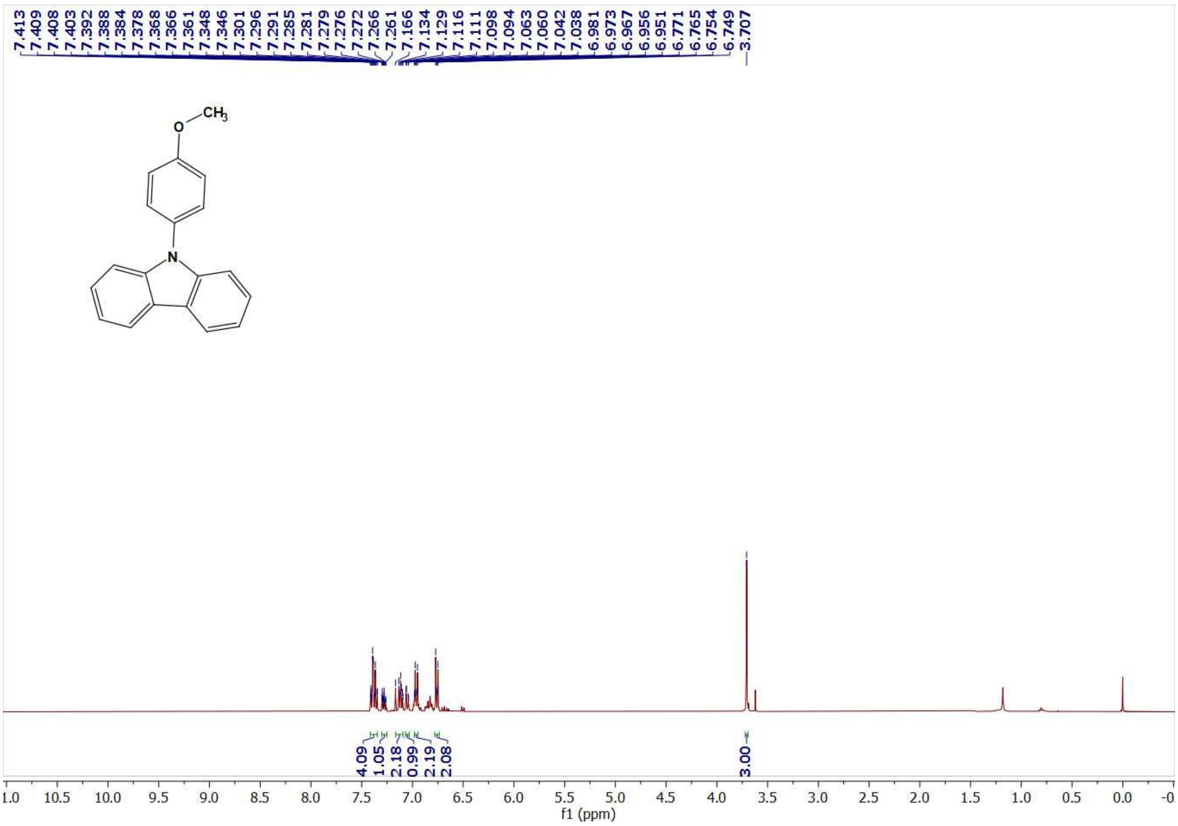


Fig. S10: ^{1}H-NMR spectra of 3b compound [400 MHz]

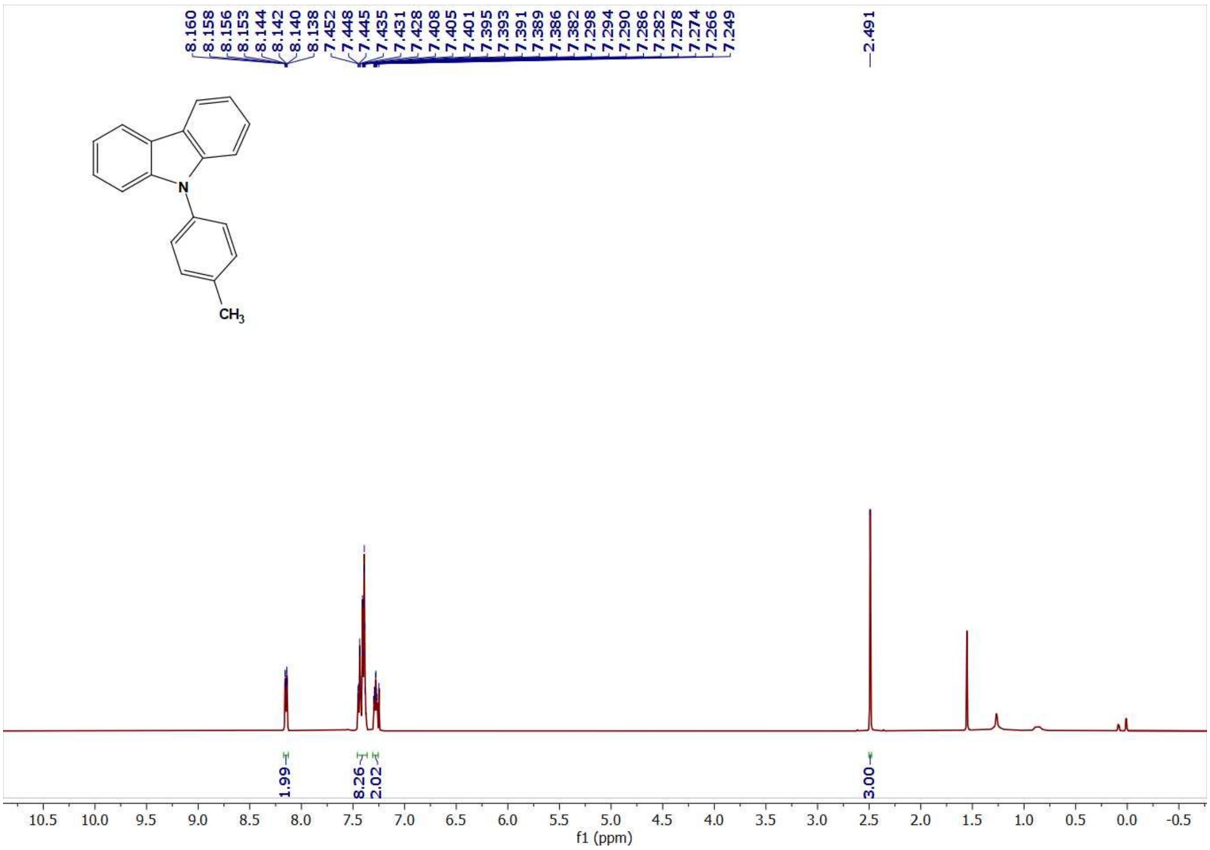


Fig. S11: ^{1}H-NMR spectra of 3c compound [500 MHz]

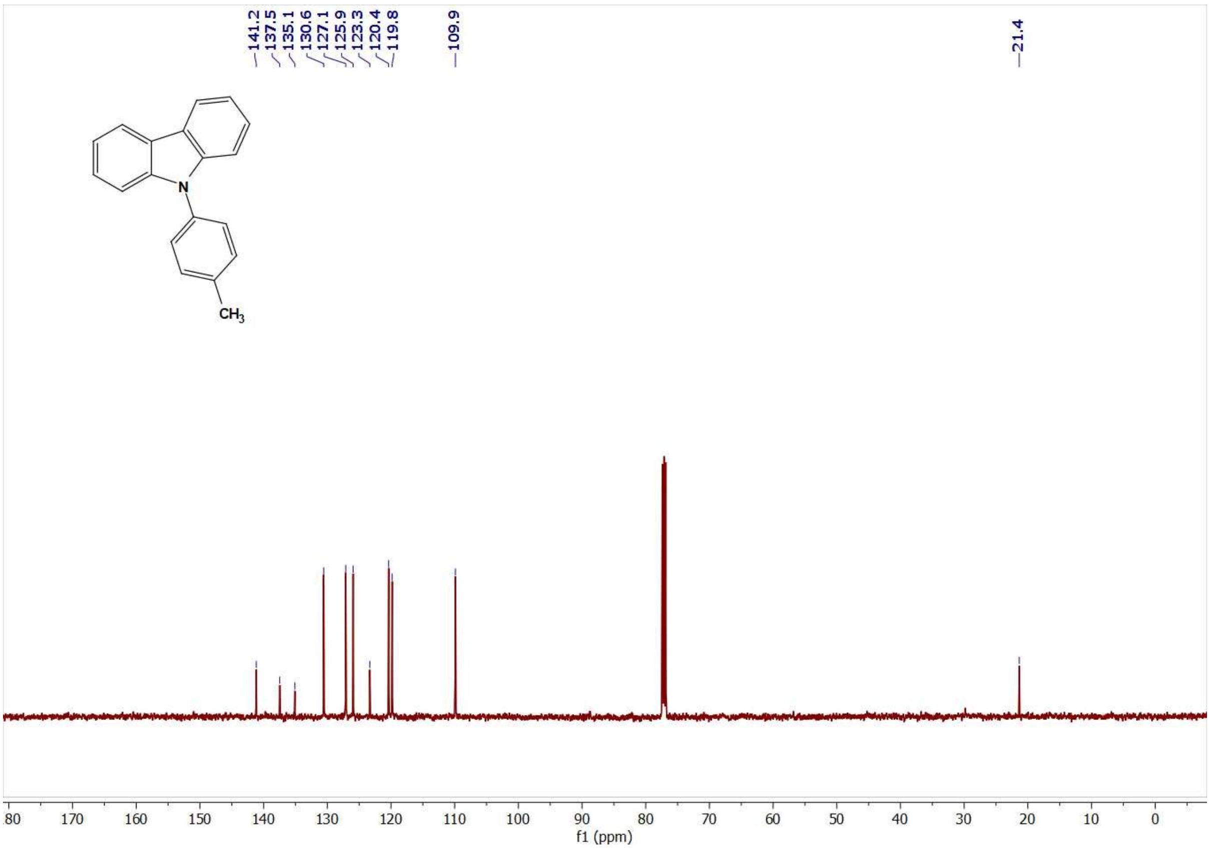


Fig. S12: ^{13}C-NMR spectra of 3c compound [126 MHz]

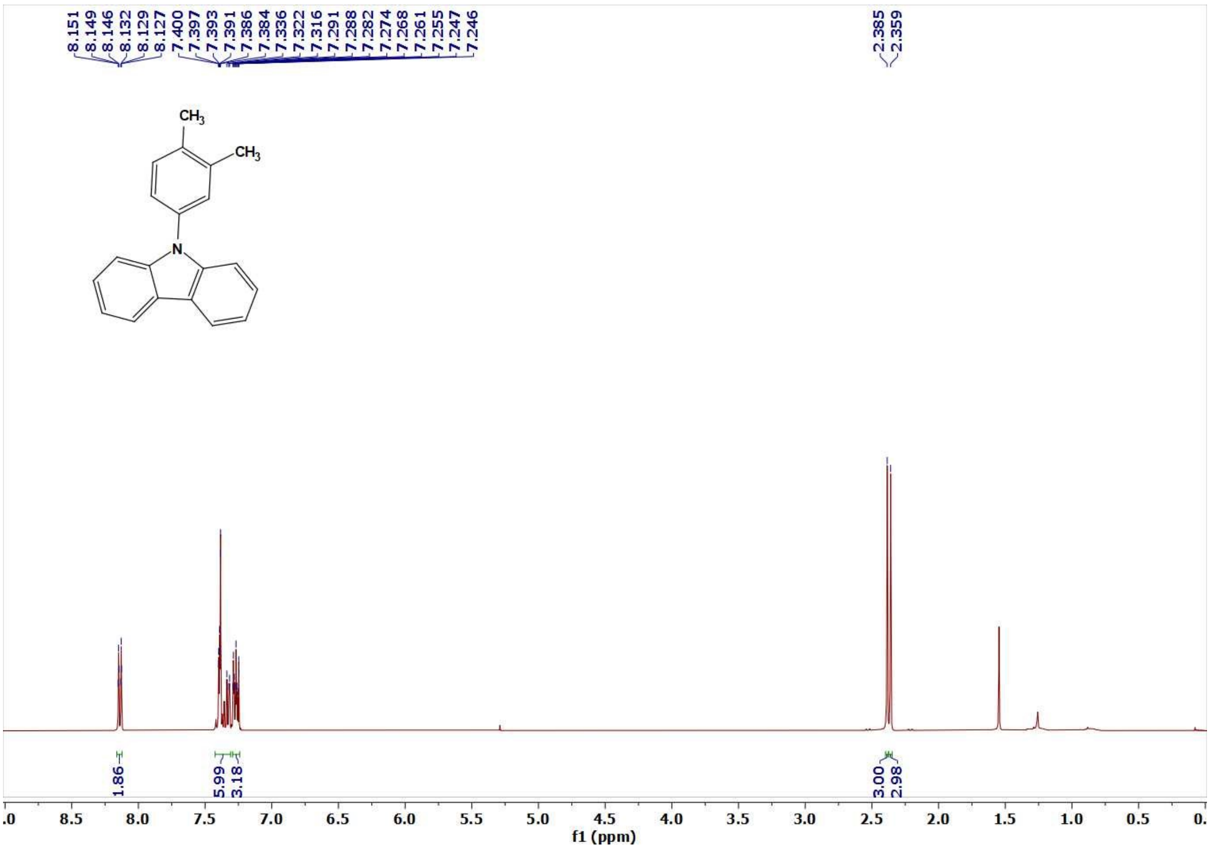


Fig. S13: ^{1}H-NMR spectra of 3d compound [400 MHz]

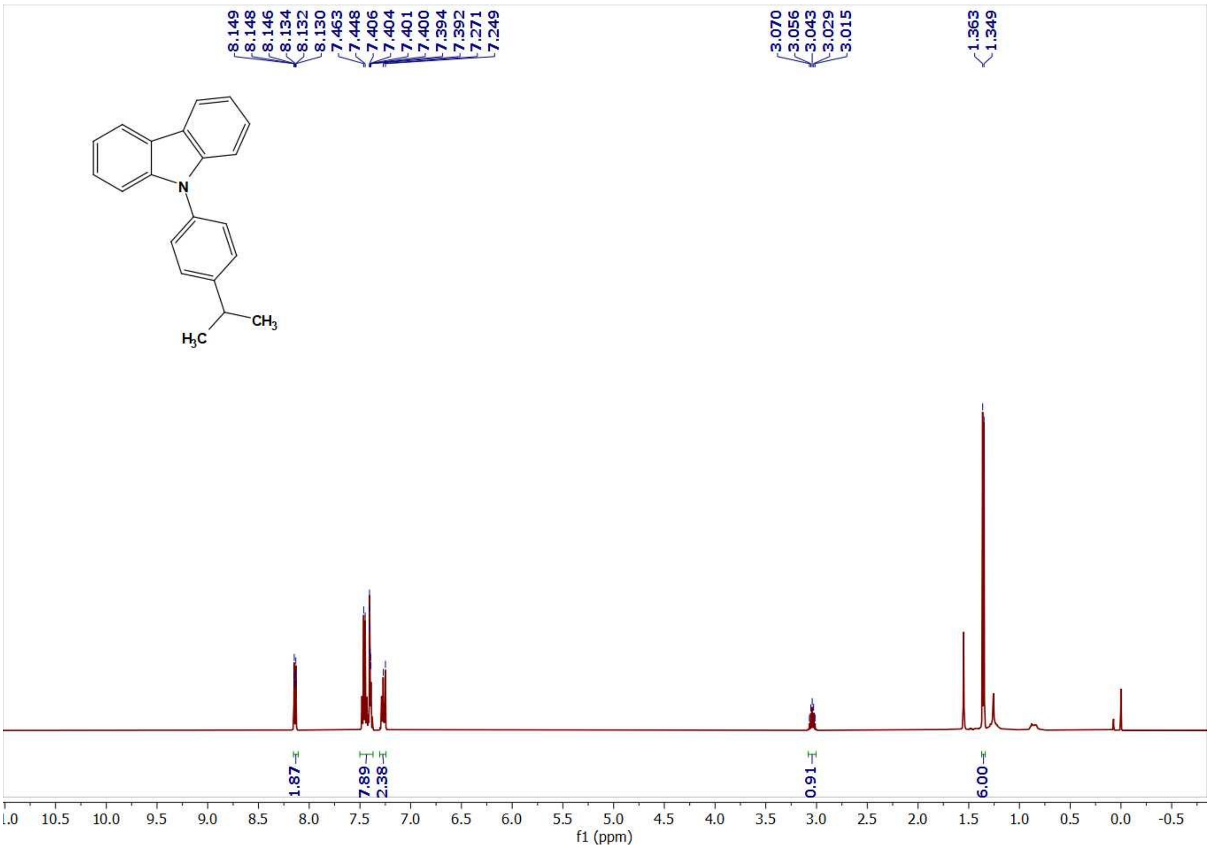


Fig. S14: ^{1}H-NMR spectra of 3e compound [500 MHz]

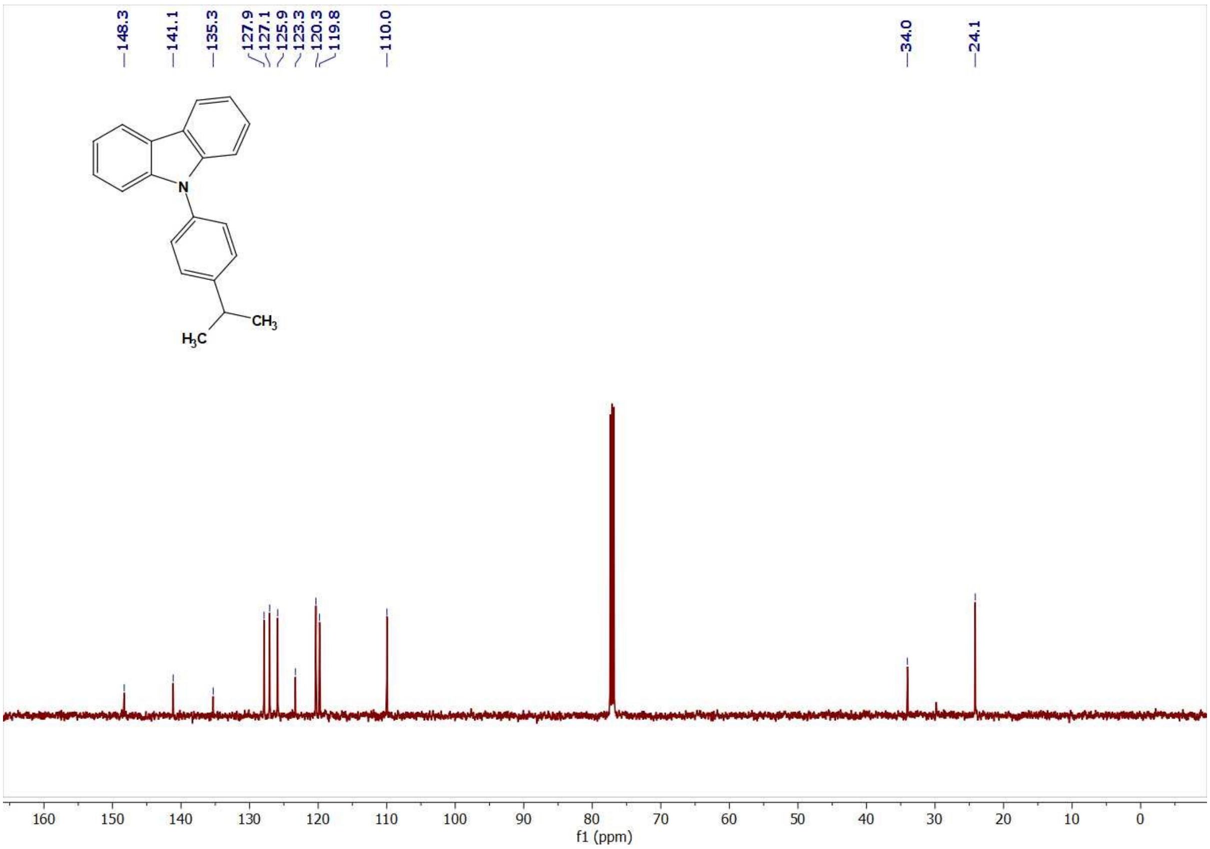


Fig. S15: ^{13}C-NMR spectra of 3e compound [126 MHz]

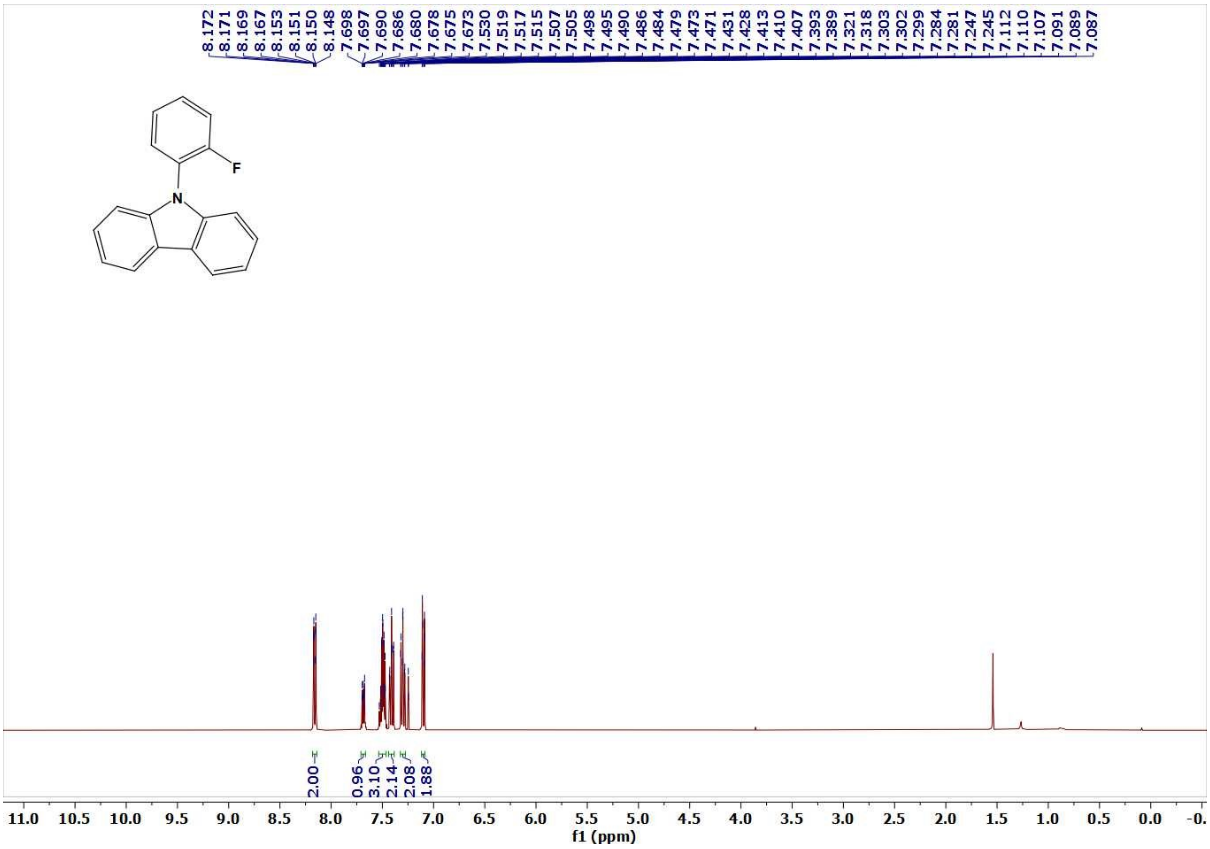


Fig. S16: ^{1}H-NMR spectra of 3f compound [400 MHz]

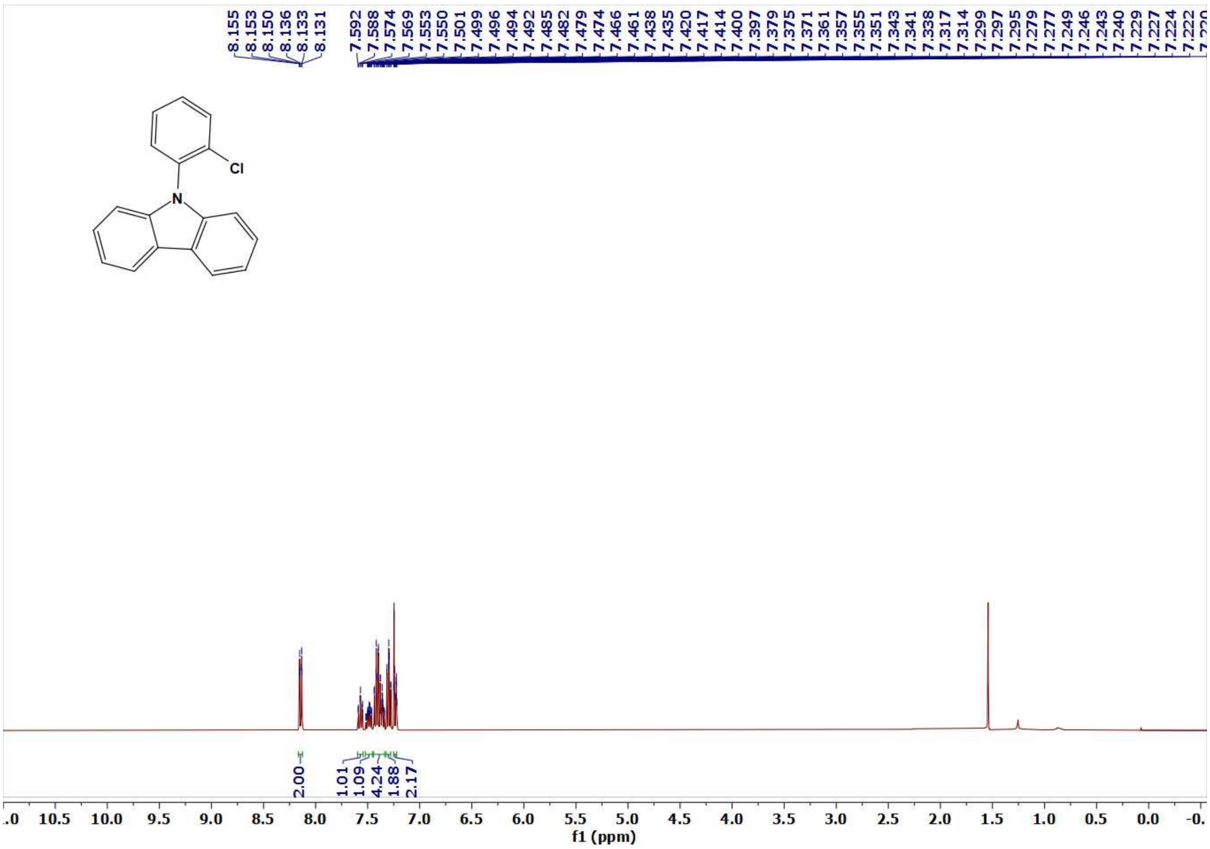


Fig. S17: ^{1}H-NMR spectra of 3g compound [400 MHz]

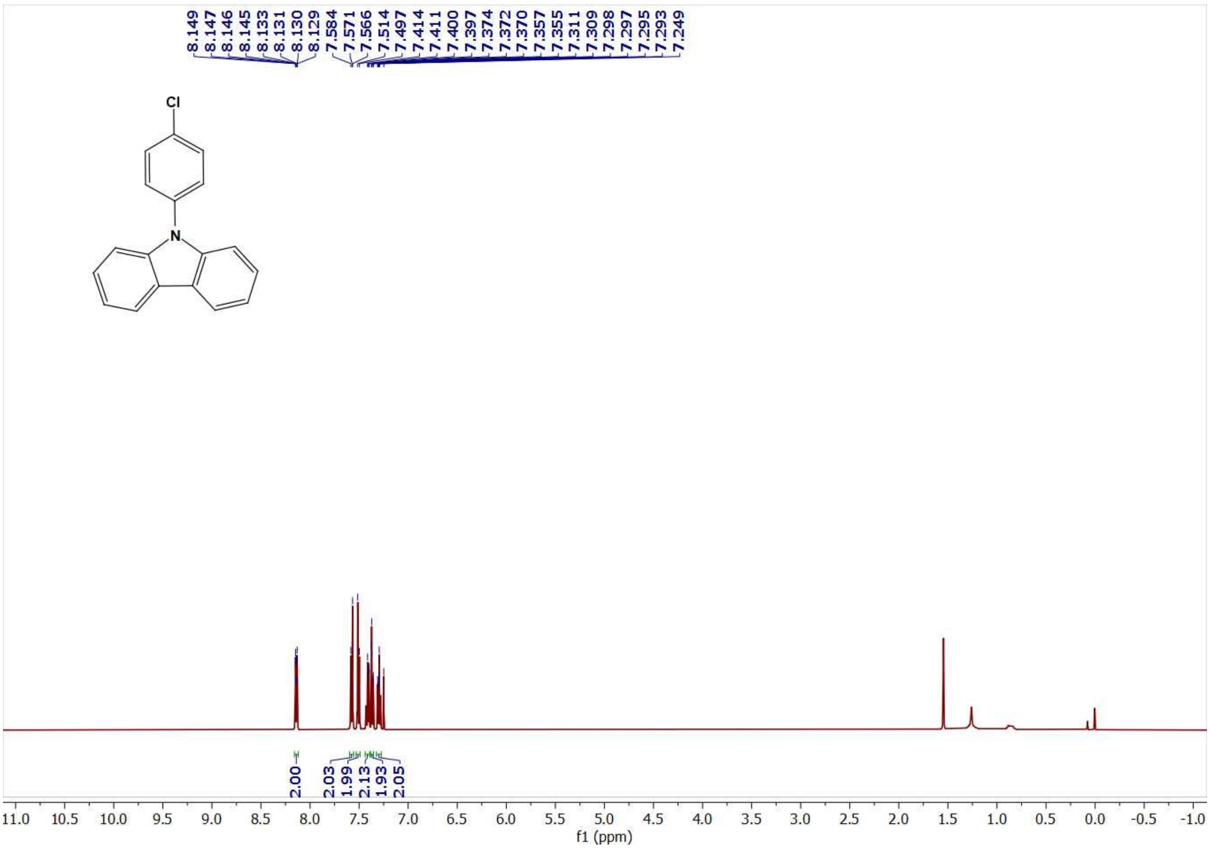


Fig. S18: ^{1}H-NMR spectra of 3h compound [500 MHz]

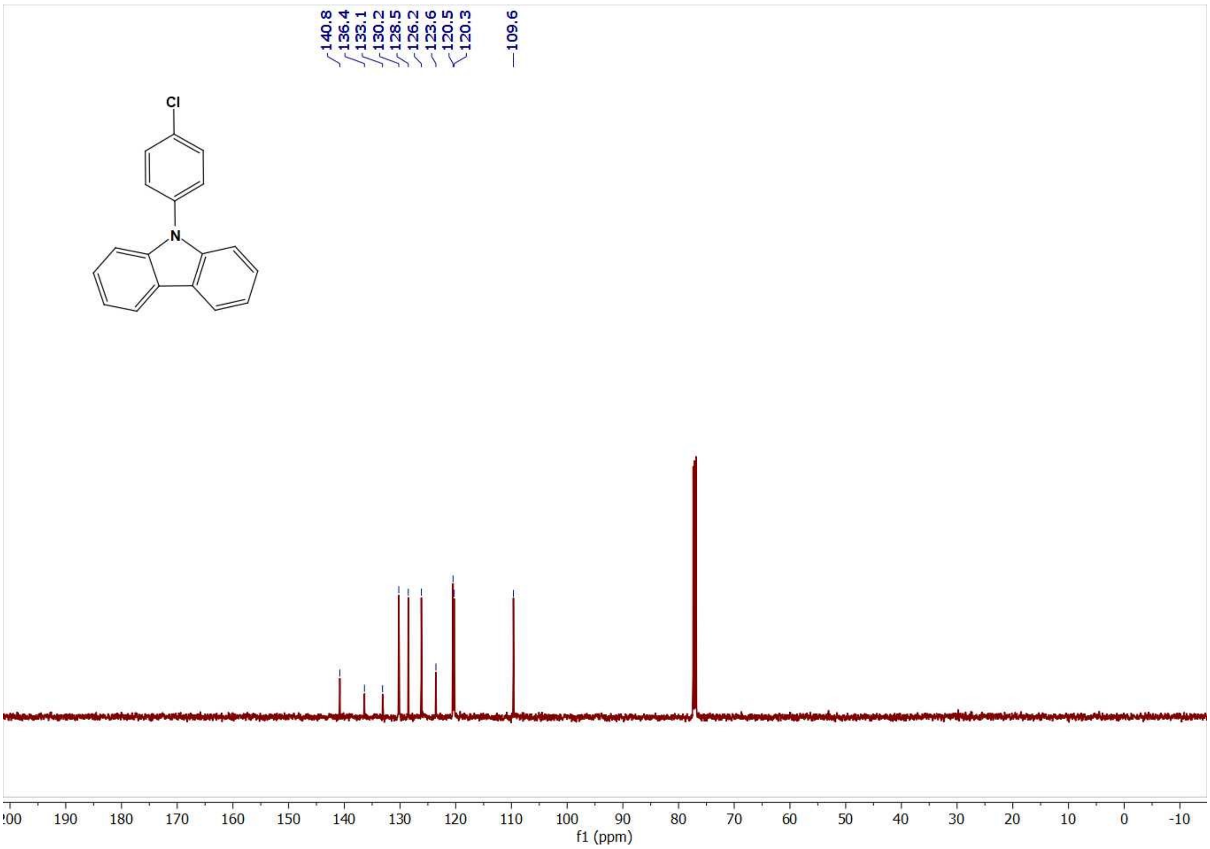


Fig. S19: ^{13}C-NMR spectra of 3h compound [126 MHz]

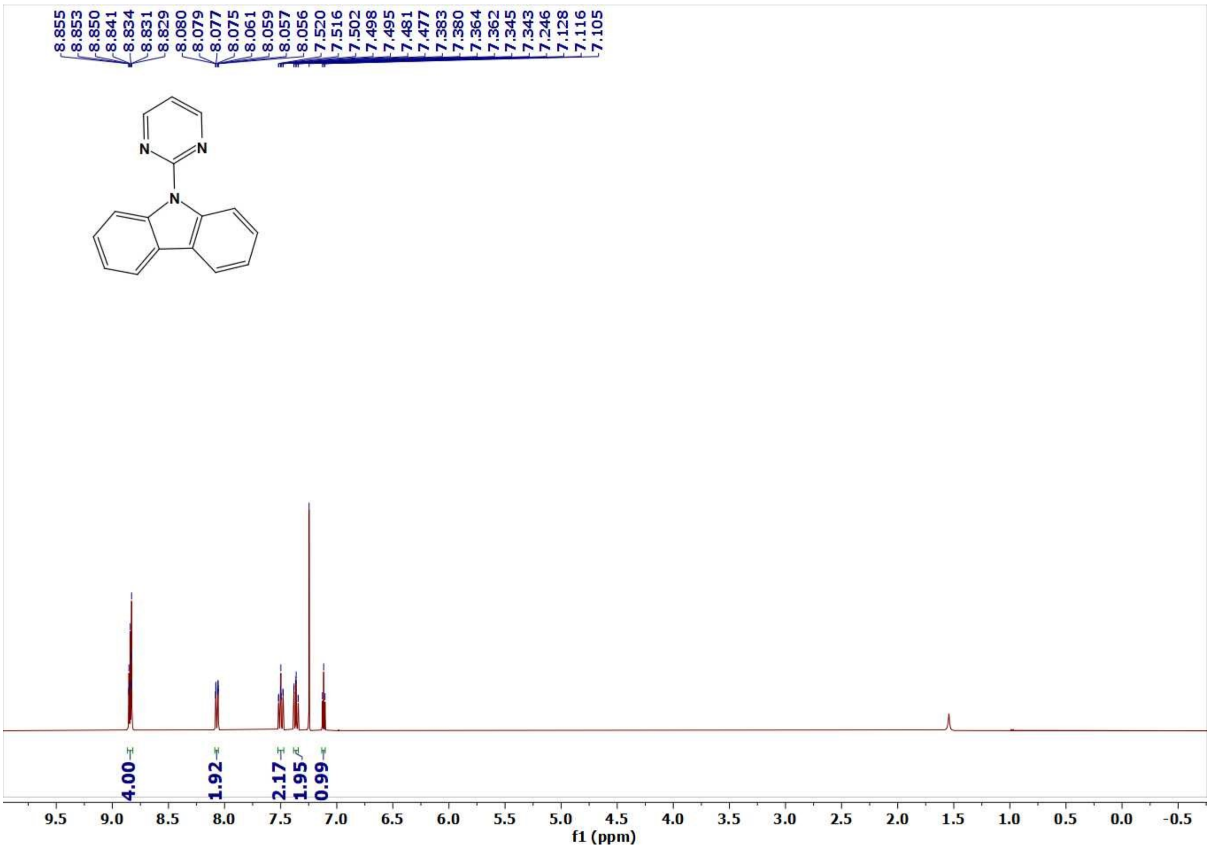


Fig. S20: ^{1}H-NMR spectra of 3i compound [400 MHz]

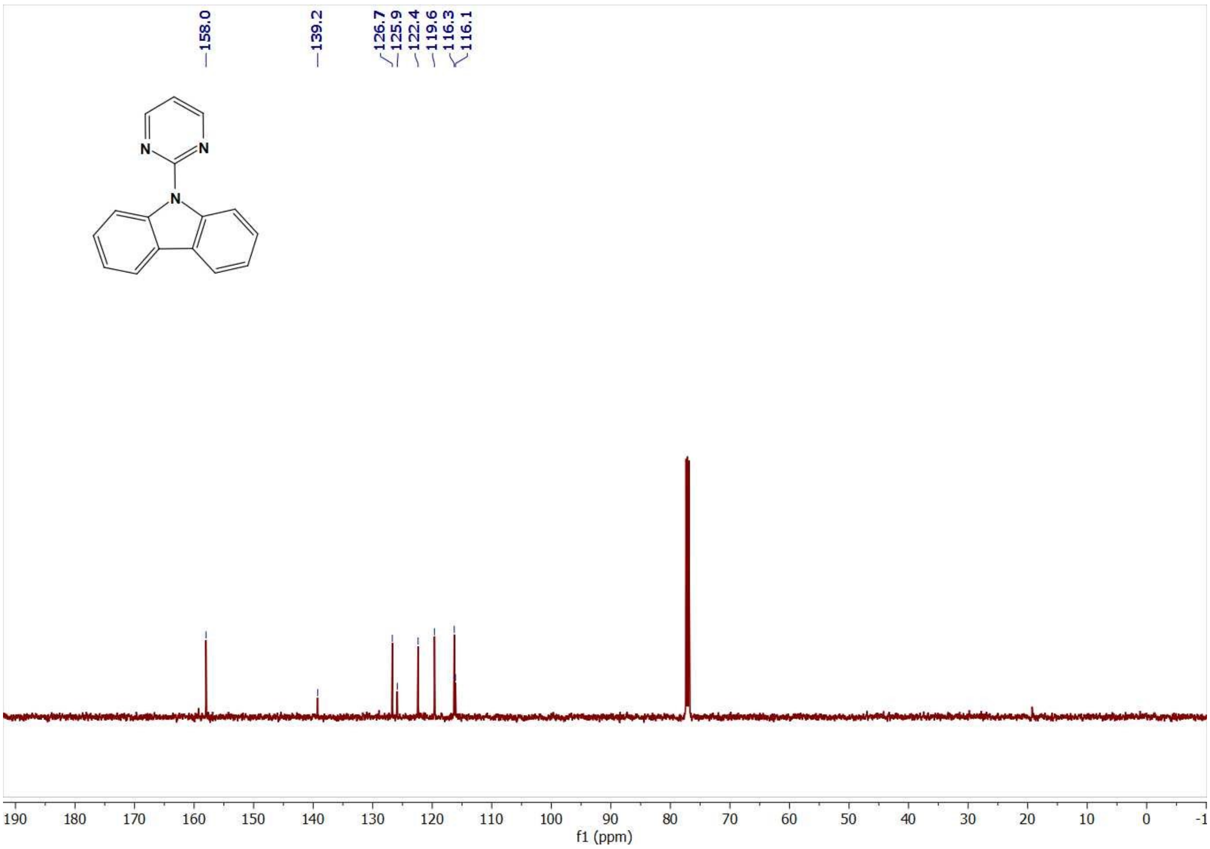


Fig. S21: ^{13}C-NMR spectra of 3i compound [126 MHz]

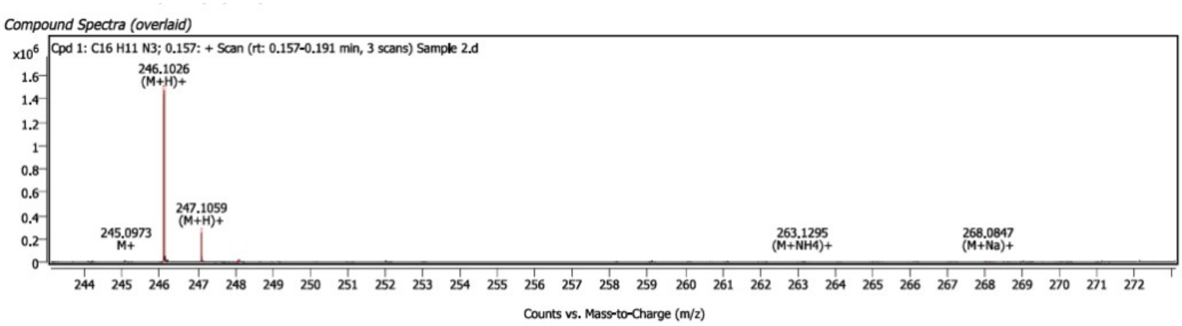


Fig. S22: ESI(+ve) mass data of 3i

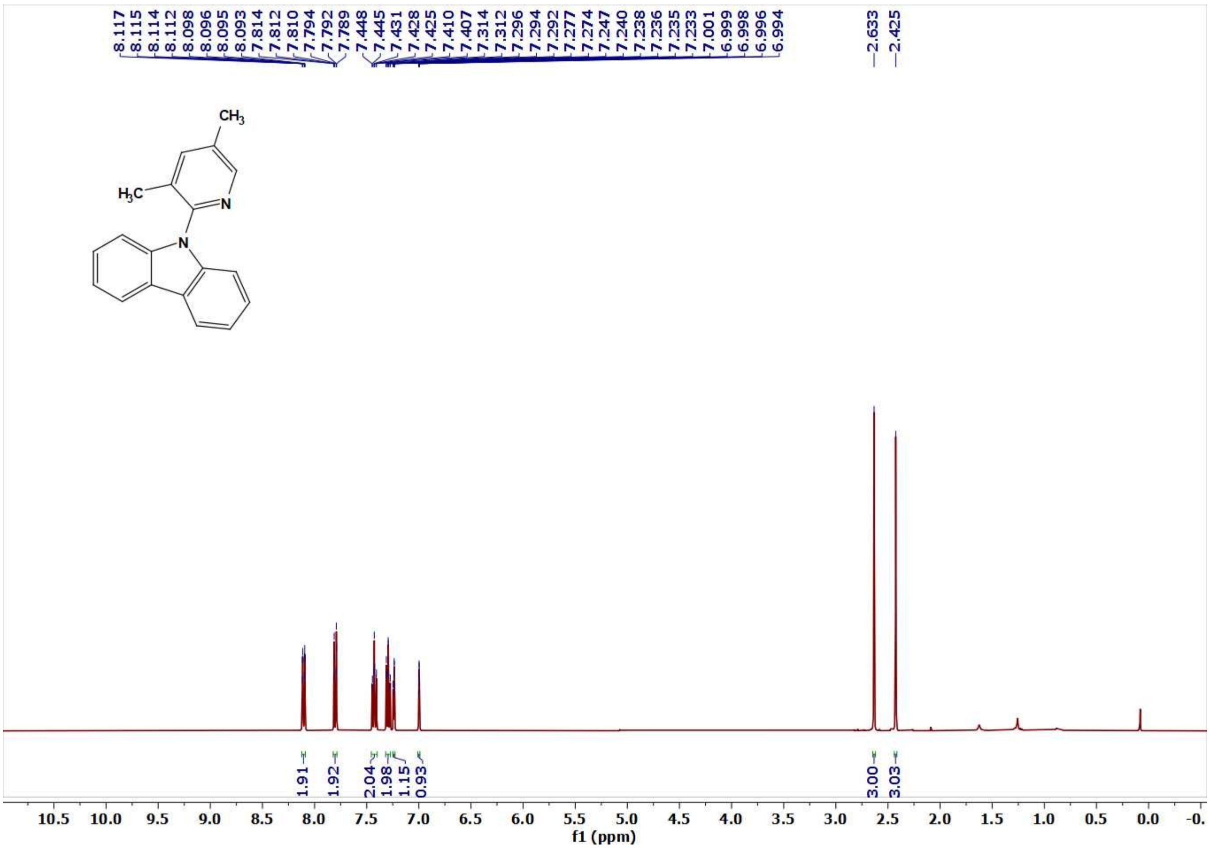


Fig. S23: ^{1}H-NMR spectra of 3j compound [400 MHz]

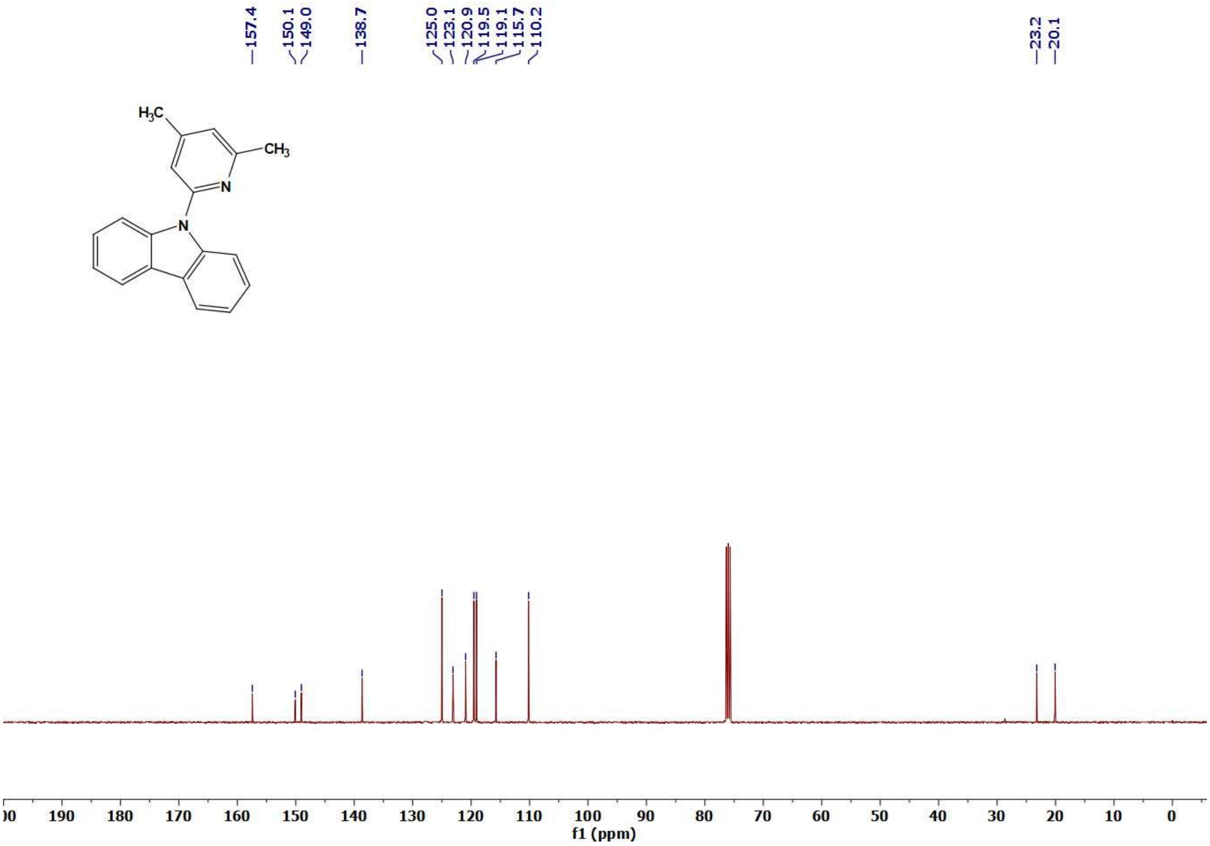


Fig. S24: ^{13}C-NMR spectra of 3j compound [101 MHz]

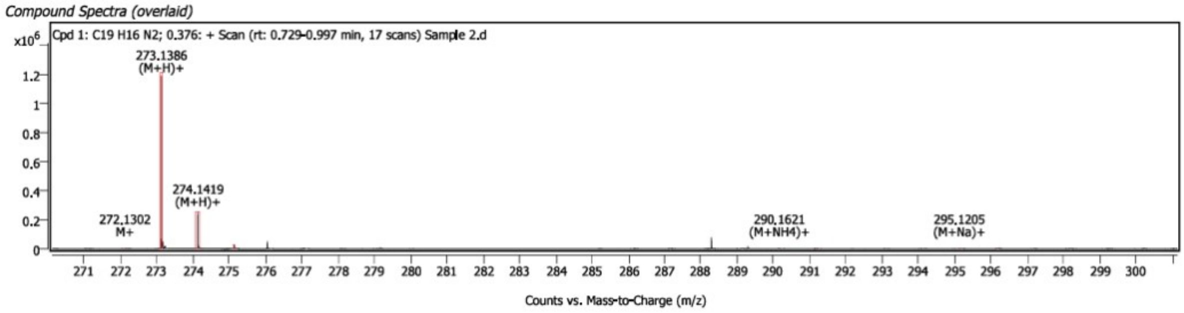


Fig. S25: ESI(+ve) mass data of 3j

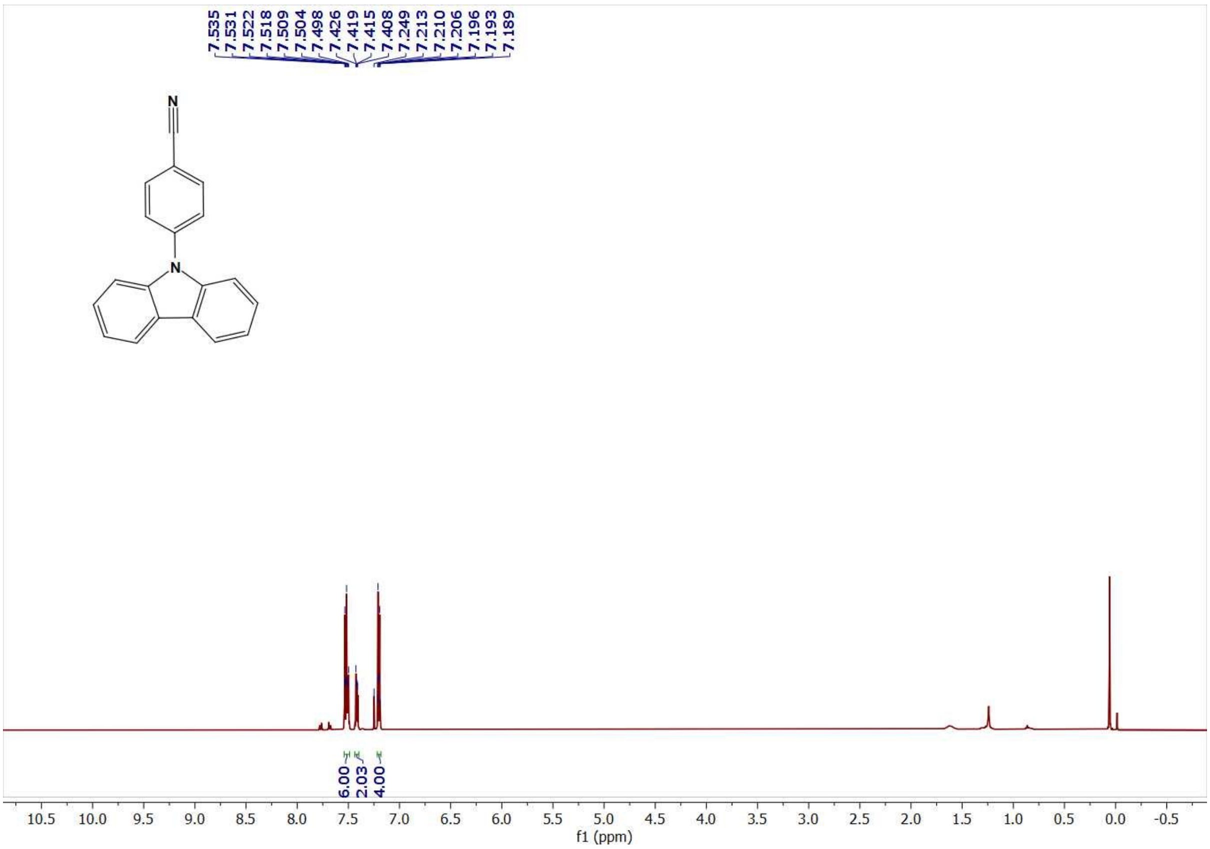


Fig. S26: ^{1}H-NMR spectra of 3k compound [500 MHz]

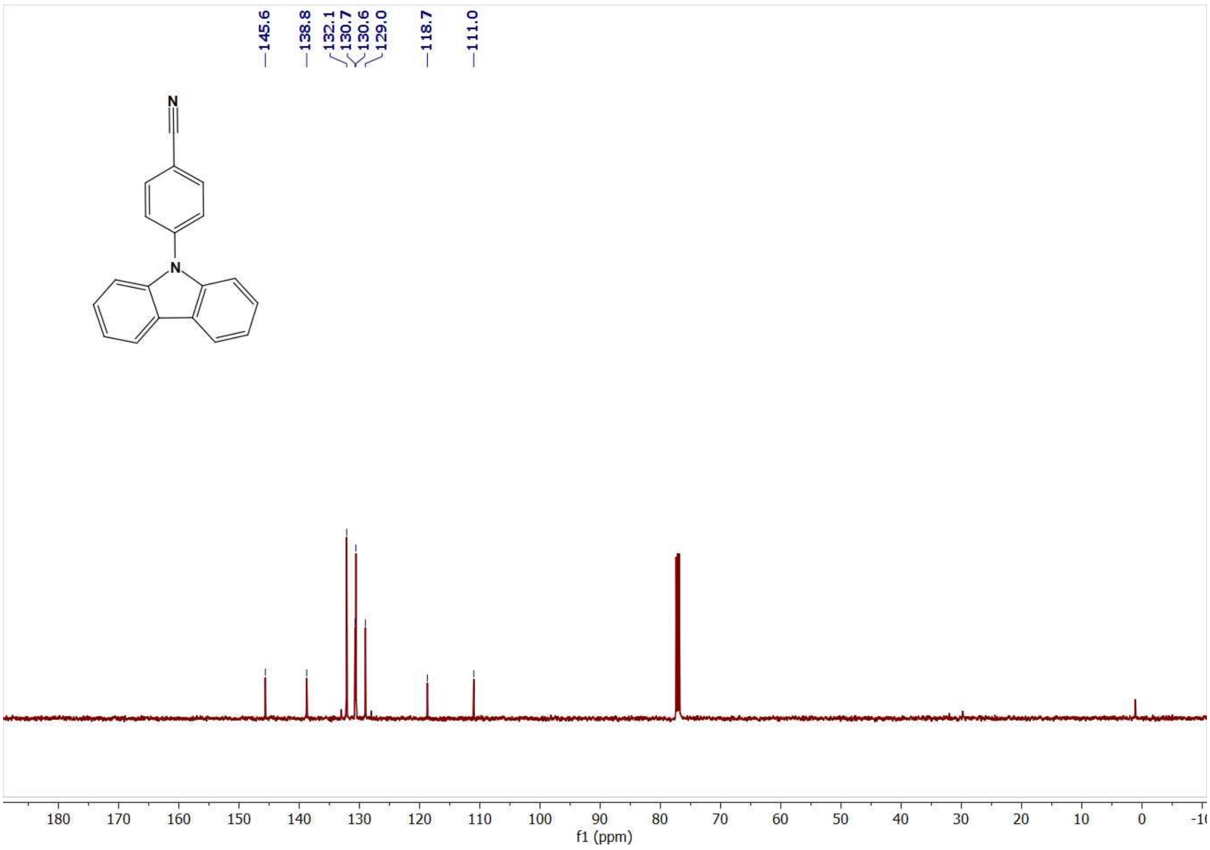


Fig. S27: ^{13}C-NMR spectra of 3k compound [126 MHz]

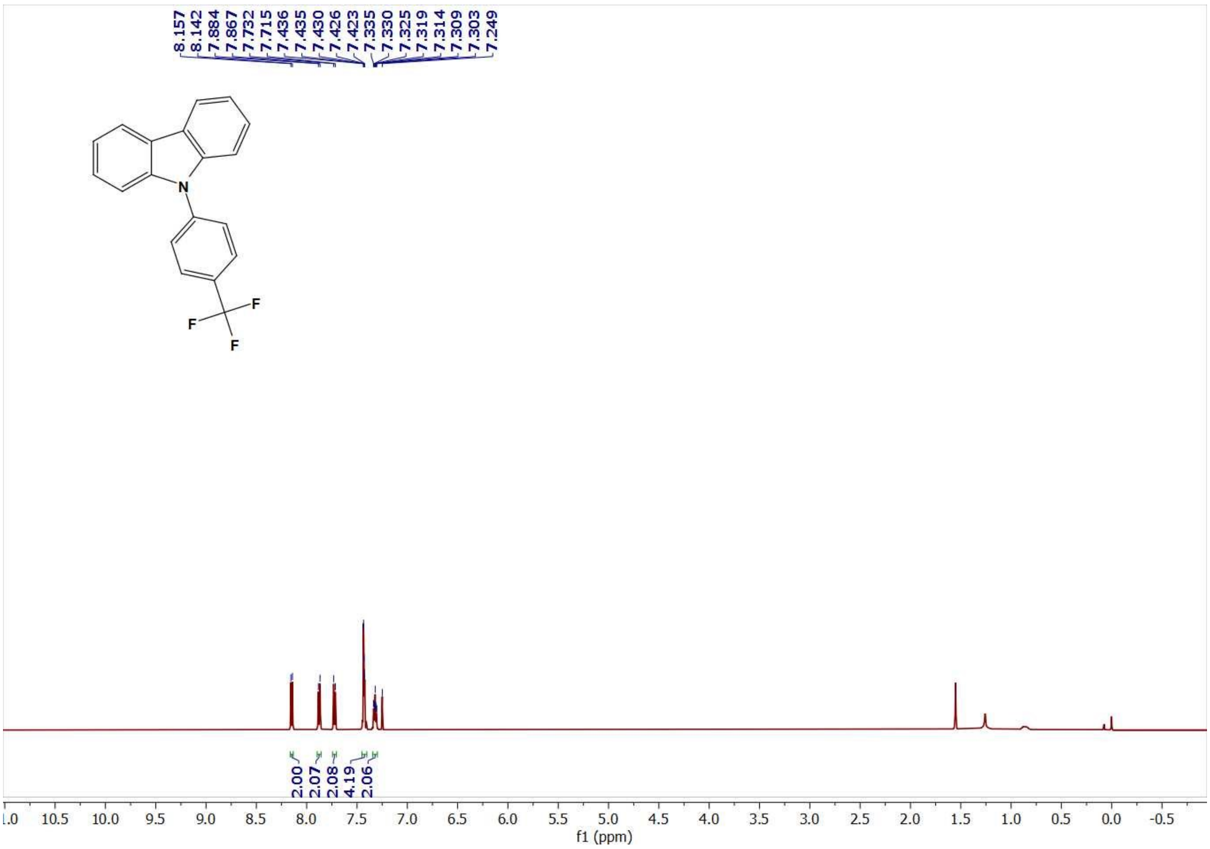


Fig. S28: ^{1}H-NMR spectra of 3l compound [500 MHz]

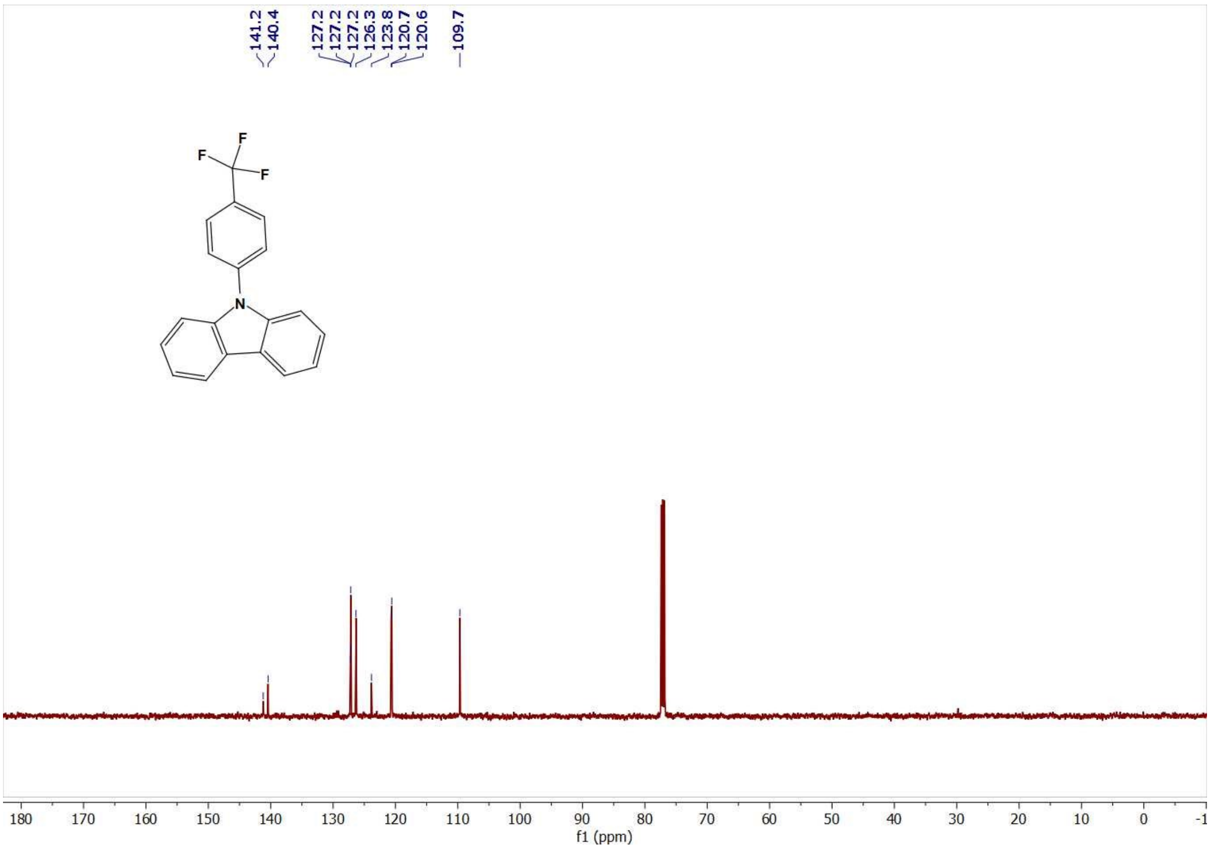


Fig. S29: ^{13}C-NMR spectra of 3l compound [126 MHz]

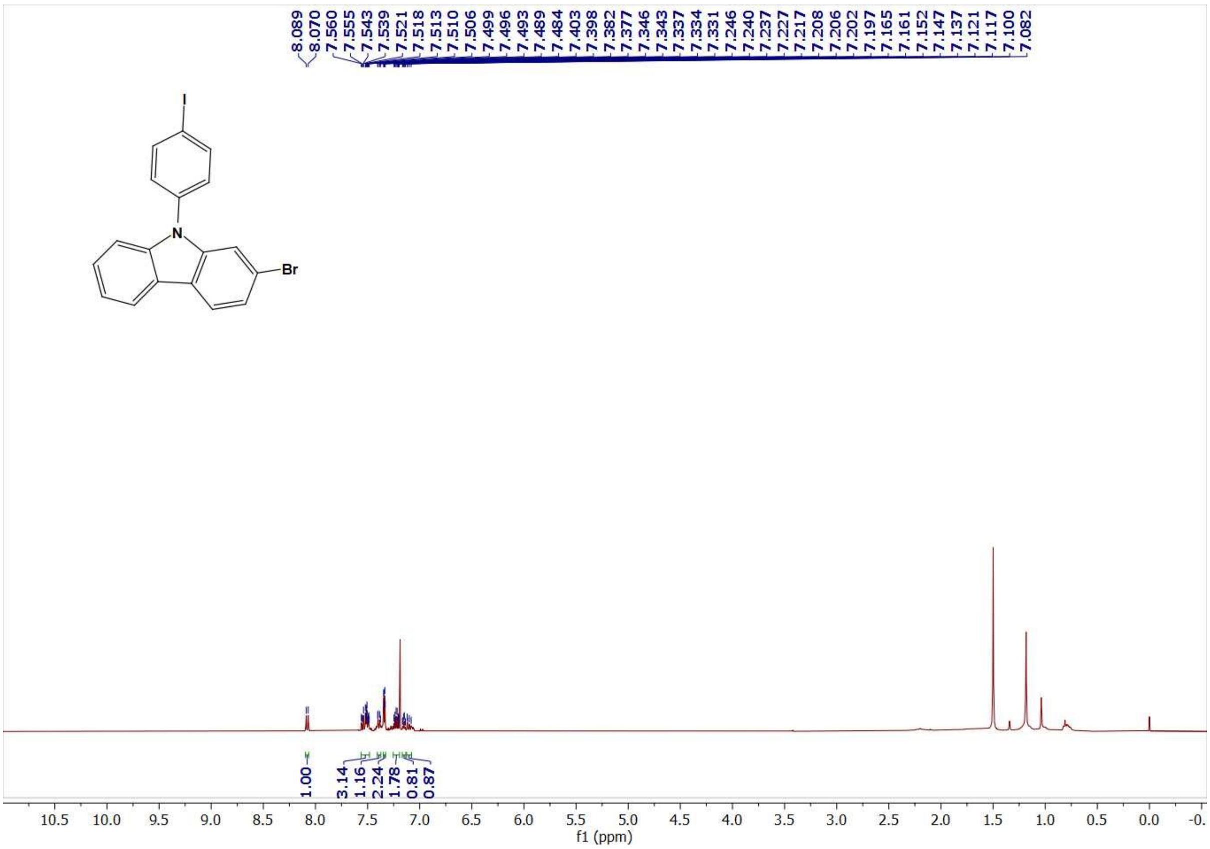


Fig. S30: ^{1}H-NMR spectra of 3m compound [400 MHz]

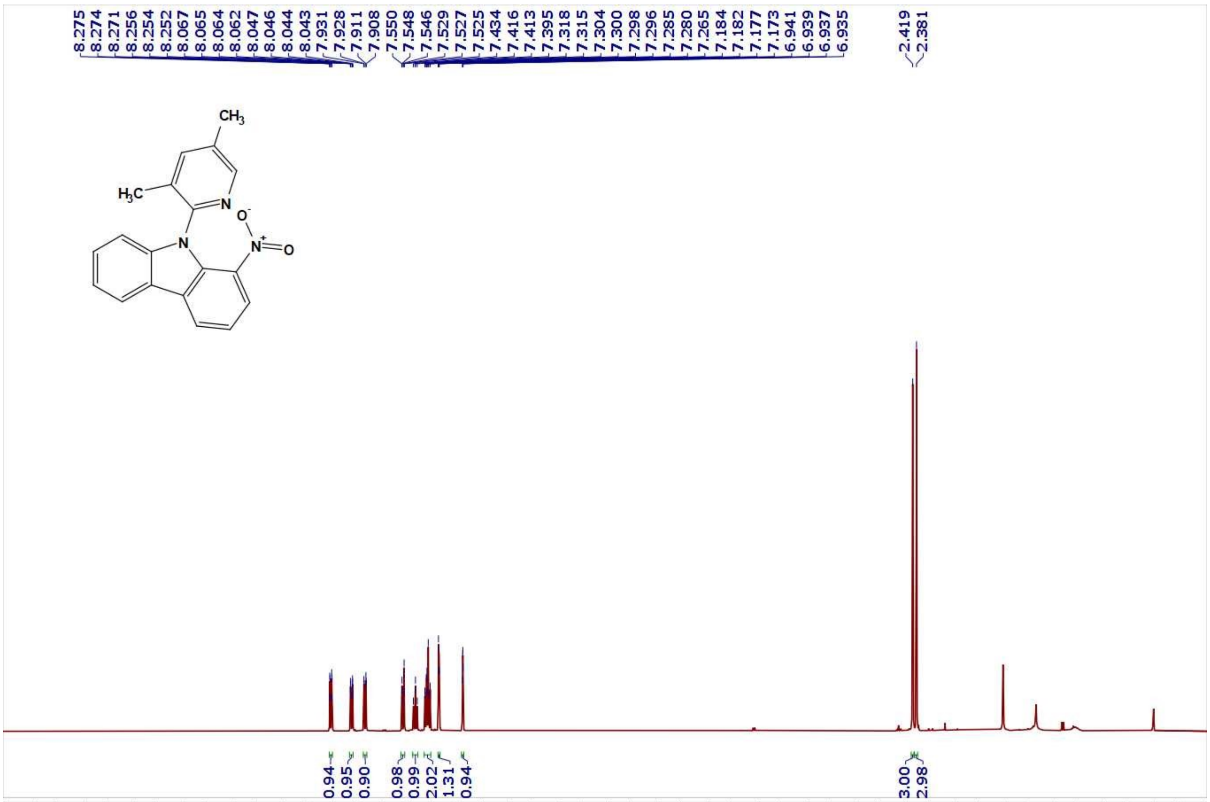


Fig. S31: ^{1}H-NMR spectra of 4a compound [400 MHz]

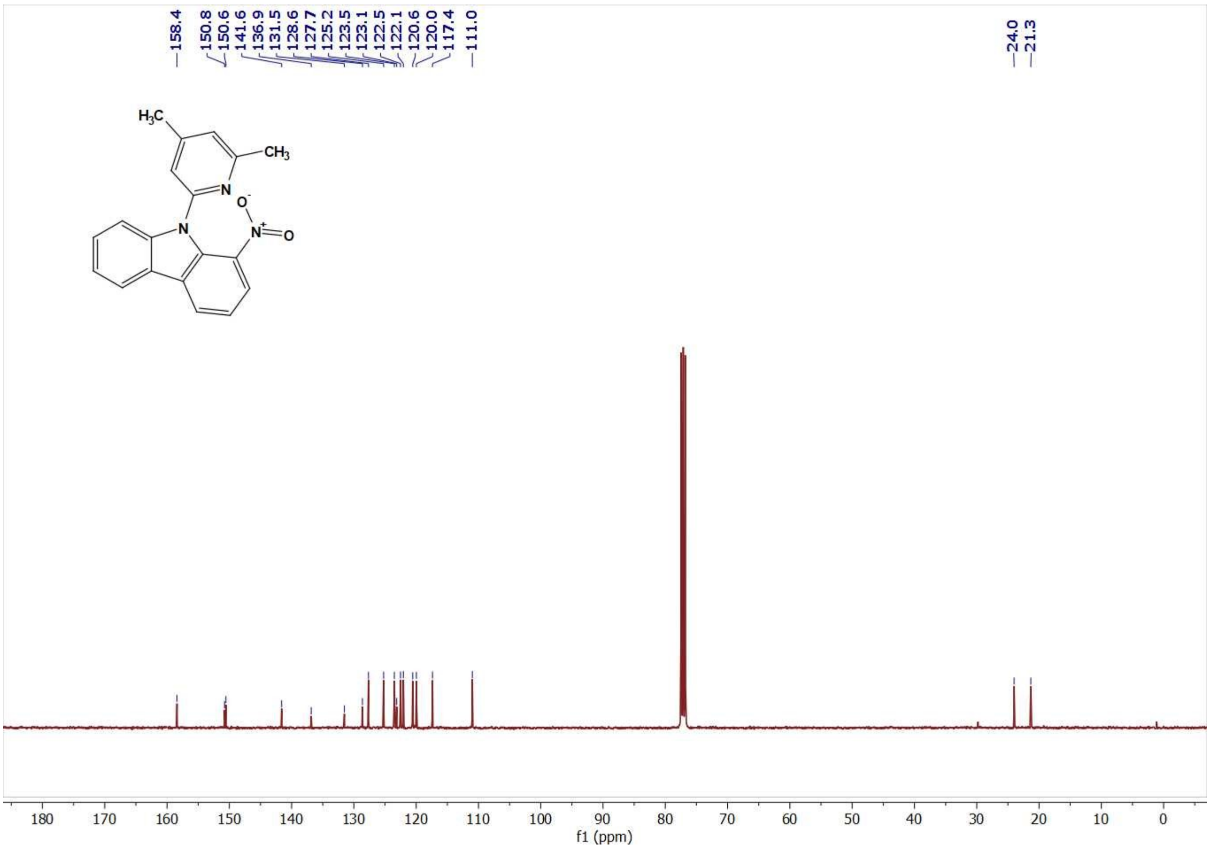


Fig. S32: ^{13}C-NMR spectra of 4a compound [101 MHz]

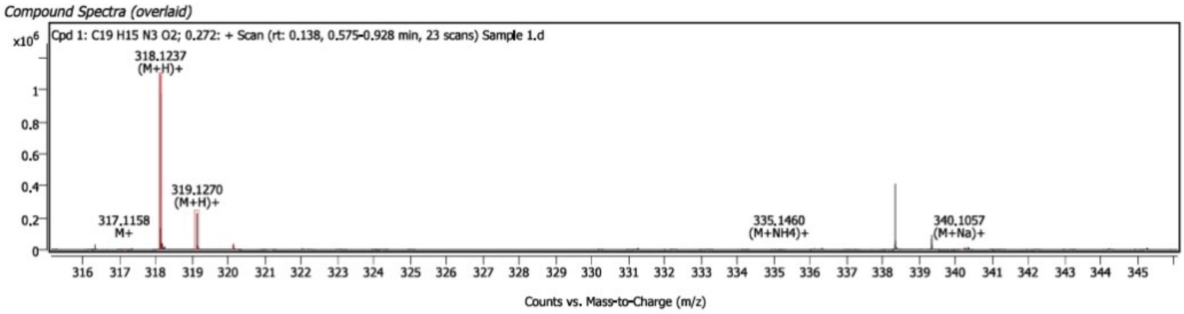


Fig. S33: ESI(+ve) mass data of 4a

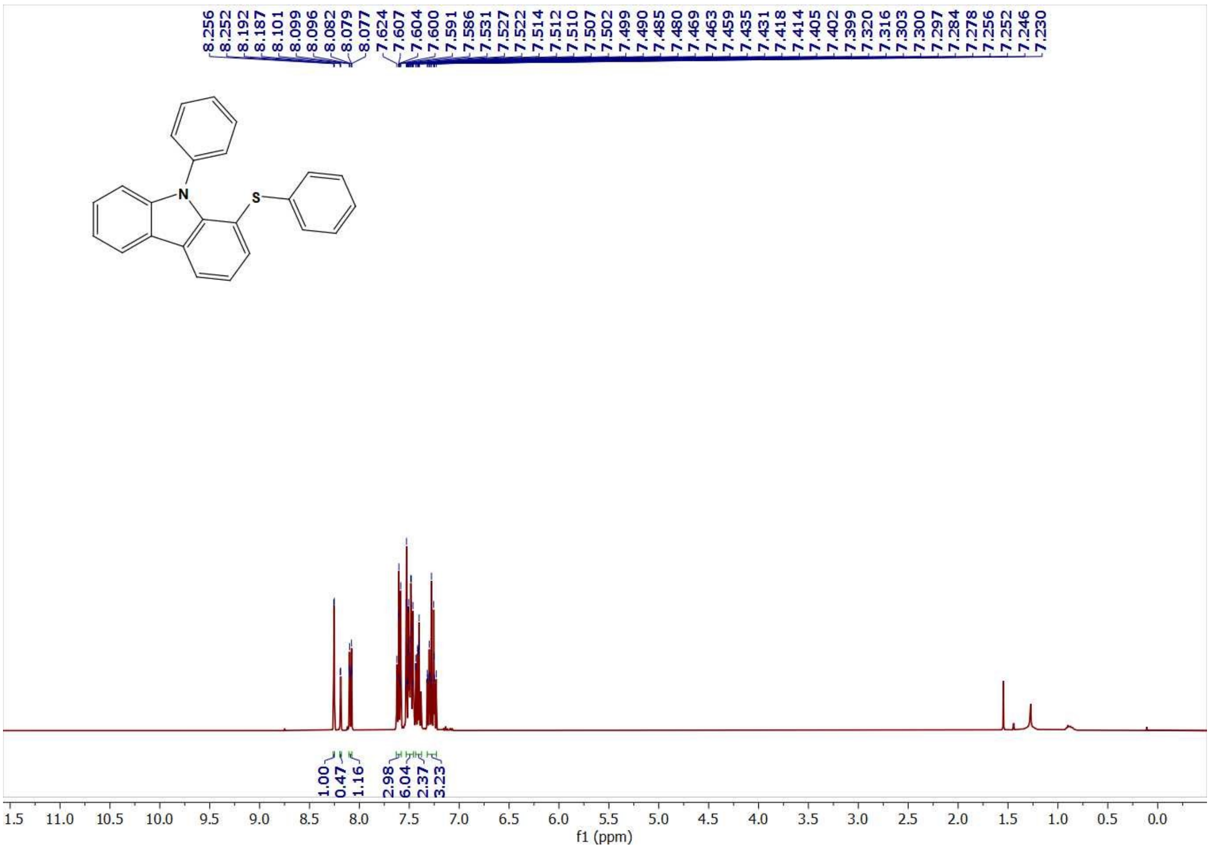


Fig. S34: ^{1}H-NMR spectra of 5a-S compound [400 MHz]

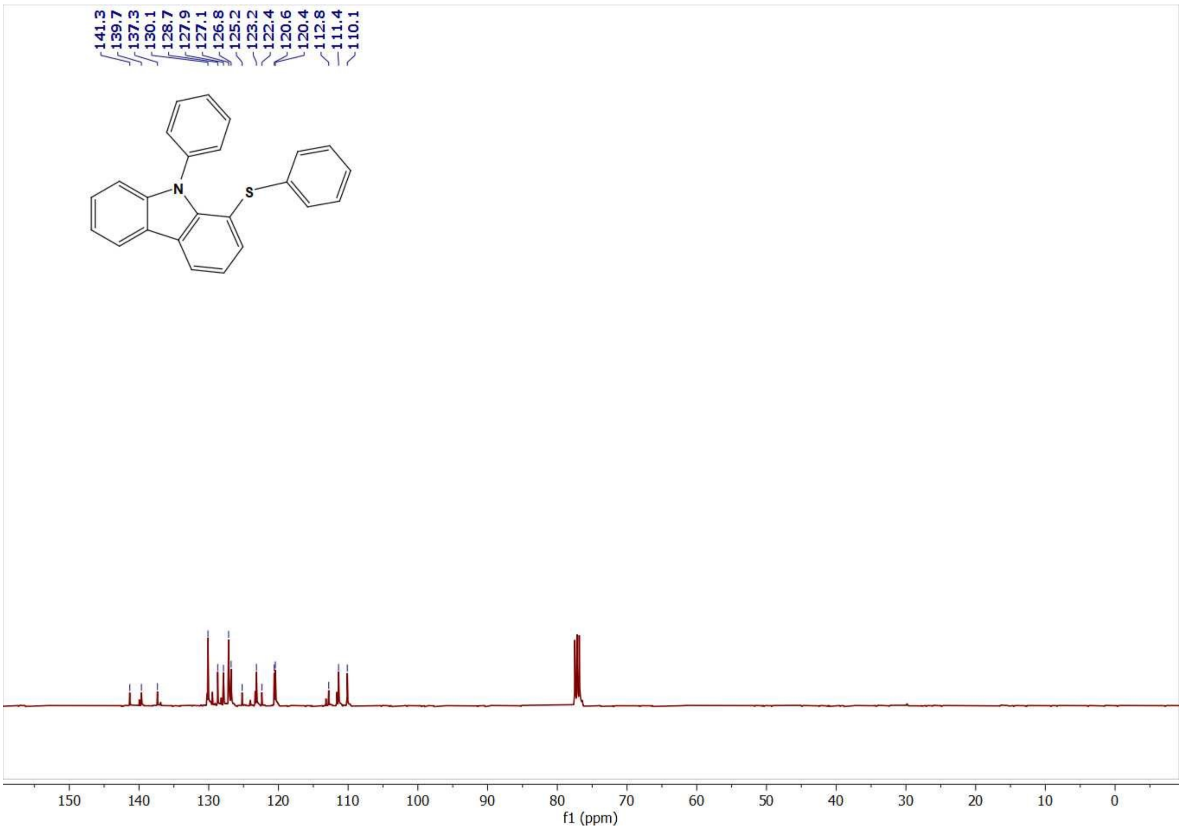


Fig. S35: ^{13}C-NMR spectra of 5a-S compound [101 MHz]

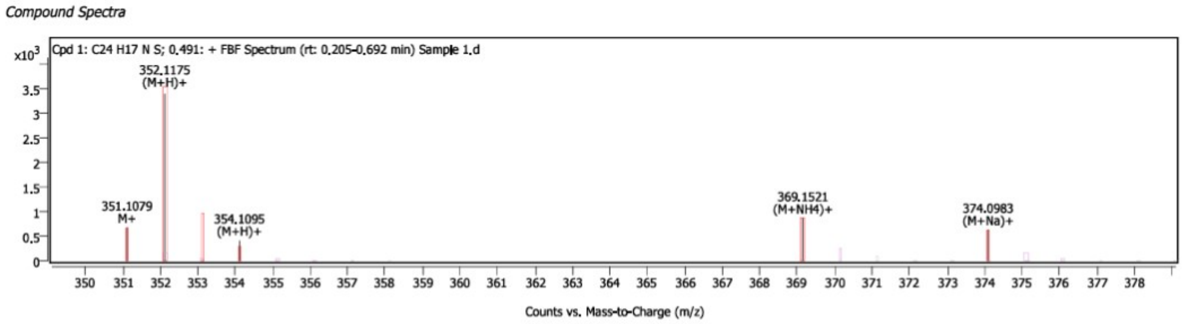


Fig. S36: ESI(+ve) mass data of 5a-S

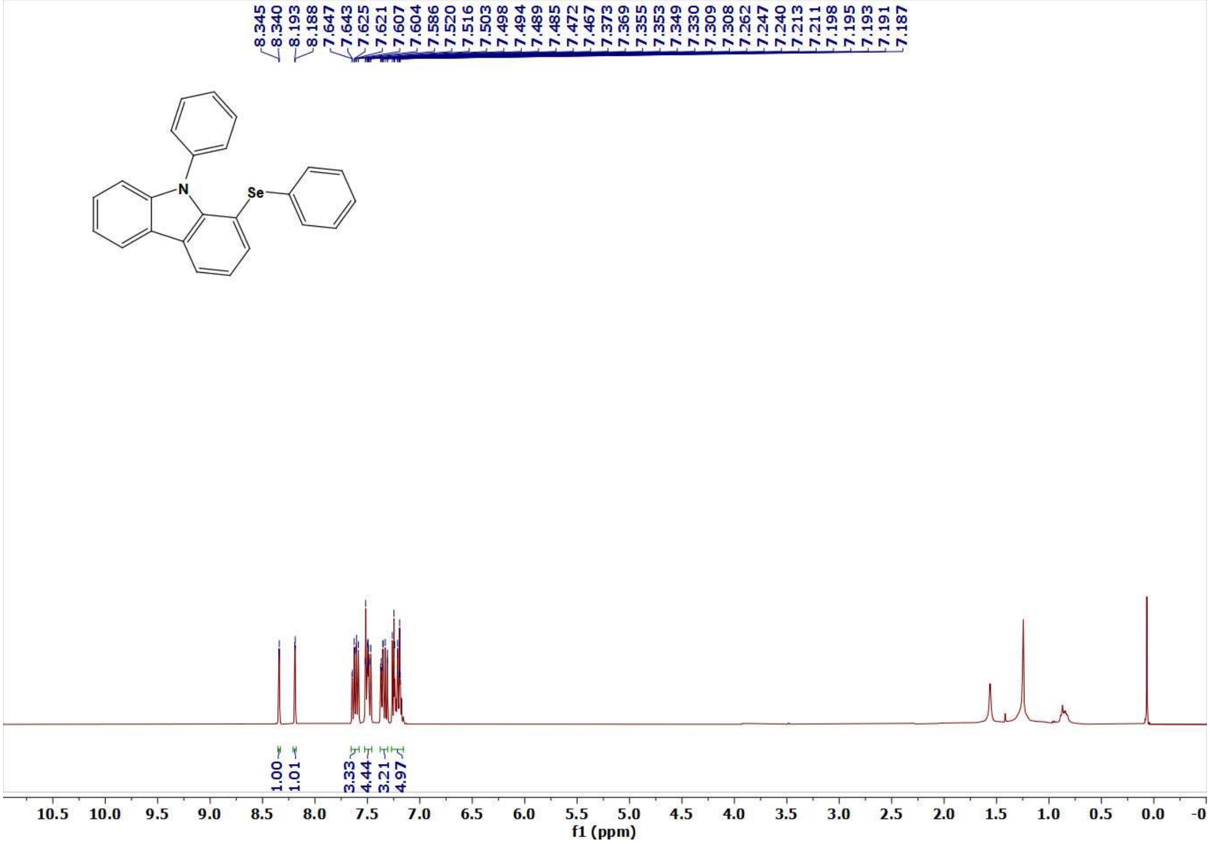


Fig. S37: ^{1}H-NMR spectra of 5a-Se compound [400 MHz]

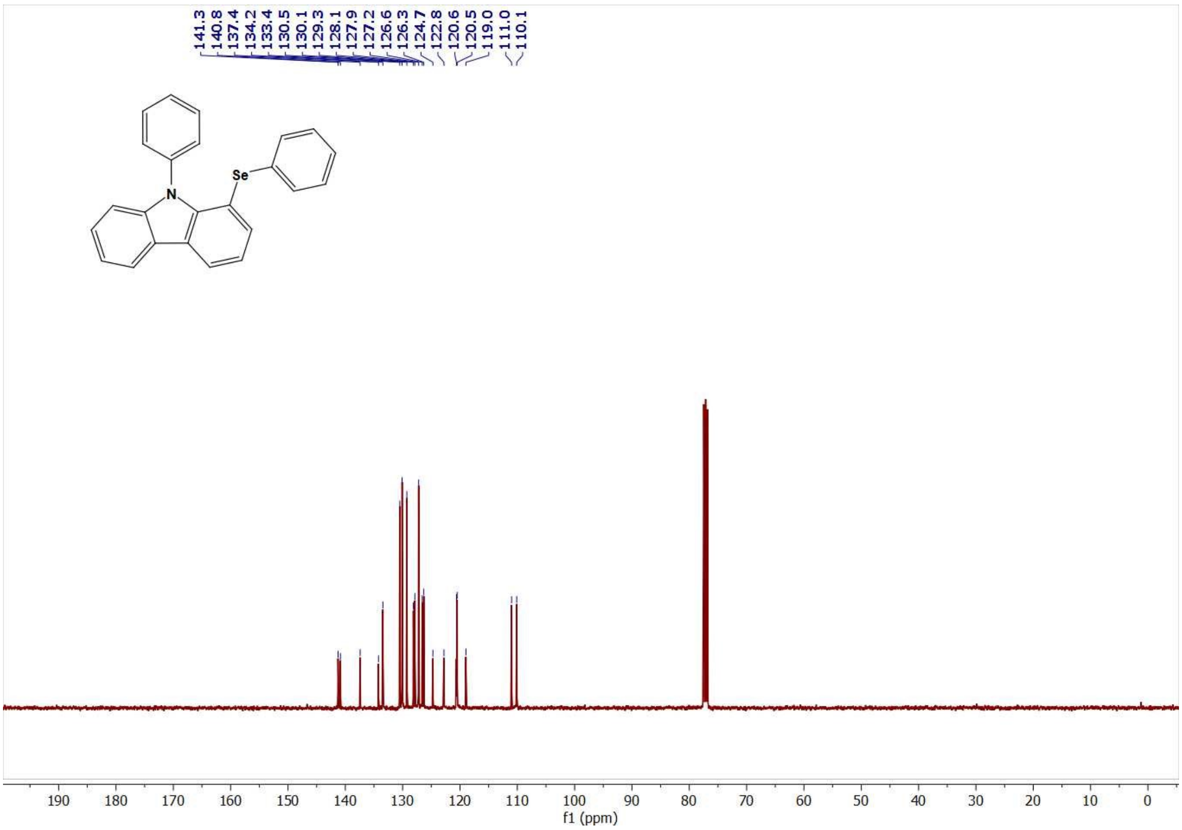


Fig. S38: ^{13}C-NMR spectra of 5a-Se compound [101 MHz]

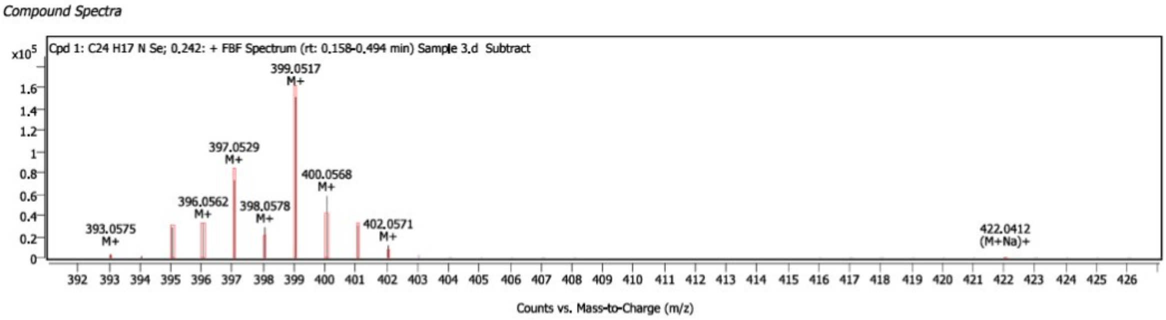


Fig. S39: ESI(+ve) mass data of 5a-Se

8 References:

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